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Impact of CB6r5 Mechanism Changes on Air Pollutant Modeling in Texas

Final Report

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RAMBOLL

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Final Report

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LIST OF ACRONYMS AND ABBREVIATIONS

CAMS	Continuous Ambient Monitoring Stations
CAMx	Comprehensive Air quality Model with extensions
CPA	Chemical Process Analysis
CB6	Carbon Bond mechanism Version 6
CB6r4	Carbon Bond mechanism Version 6 Revision 4
CB6r5	Carbon Bond mechanism Version 6 Revision 5
DFW	Dallas-Fort Worth
EPA	Environmental Protection Agency
HO_2	Hydroperoxy radical
IUPAC	International Union of Pure and Applied Chemistry
JPL	NASA Jet Propulsion Laboratory
NAA	Non-attainment Area
NAAQS	National Ambient Air Quality Standard
NASA	National Aeronautics and Space Administration
NME	Normalized Mean Error
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx	Oxides of Nitrogen
O_3	Ozone
OH	Hydroxyl radical
PAN	Peroxyacetyl nitrate
RO_2	Organic peroxy radical
SIP	State Implementation Plan
TCEQ	Texas Commission on Environmental Quality
VOC	Volatile Organic Compounds

EXECUTIVE SUMMARY

The Texas Commission on Environmental Quality (TCEQ) uses the Comprehensive Air Quality Model with Extensions (CAMx) to predict future ozone concentrations for State Implementation Plan (SIP) purposes. The most recent version of the Carbon Bond (CB) chemical mechanism in CAMx (called CB6r4) was developed in the past decade. However, the core inorganic reactions involving nitrogen oxides (NOx), ozone, and the hydroxyl radical have not been updated since 2011. In addition, the modeling and analysis performed under a recent Texas Air Quality Research Program project showed that many of these core reactions are important and that uncertainties in their rates cause the most uncertainty in the ozone chemistry (Dunker et al., 2020). This project updated the CB6r4 reactions of inorganic and simple organic species that play a role in ozone formation, prioritizing the reactions that cause the most uncertainty in the modeling results. The updated mechanism is revision 5 of the Carbon Bond 6 mechanism, namely CB6r5.

We performed an extensive literature review of rate constants used in the CB6r4 mechanism that considered 152 of the 233 reactions in CB6r4. We revised reaction rates for 47 reactions and added one new reaction to create CB6r5. CB6r5 tends to predict higher ozone concentrations than CB6r4 although CB6r5 has lower ozone over portions of the Gulf of Mexico. Chemically, the ozone changes due to CB6r5 updates are associated with small changes (increases) in nitrogen dioxide (NO_2) in regions where ozone production is NOx-limited. Accordingly, we conducted additional review of mechanism updates that influence NO_2 availability leading to a revised final mechanism (development version 3, CB6r5d3) with more moderate ozone increases than the initial version (CB6r5d1). Quantitative performance evaluation for 8-hour average ozone in Texas during June 2012 found that CB6r5 performs similarly to CB6r4 with statistical metrics for both mechanisms meeting the criteria recommended by Emery et al. (2017). The tendency of CB6r5 to predict slightly higher ozone than CB6r4 produced slightly more positive bias and larger error with CB6r5 than CB6r4. However, the ozone changes associated with CB6r5 updates are too small for ozone model performance evaluation to assess their validity, when taking into consideration that models have uncertainties other than the chemistry (Dunker et al., 2020) including emissions, boundary concentrations, deposition and meteorology. We recommend additional testing and evaluation to understand how CB6r5 mechanism updates influence CAMx model performance for ozone.

1.0 INTRODUCTION

The Texas Commission on Environmental Quality (TCEQ) uses the Comprehensive Air Quality Model with Extensions (CAMx) to predict future ozone concentrations for State Implementation Plan (SIP) purposes. The most recent version of the Carbon Bond (CB) chemical mechanism in CAMx (called CB6r4) was developed in the past decade, and the most recent updates include reactions leading to ozone destruction by iodine emissions from the Gulf of Mexico. However, the core inorganic reactions involving nitrogen oxides (NOx), ozone, and the hydroxyl radical have not been updated since 2011. In addition, the modeling and analysis performed under a recent Texas Air Quality Research Program project show that many of these core reactions are important and that uncertainties in their rates cause the most uncertainty in the ozone chemistry (Dunker et al., 2020). This project updated the CB6r4 reactions of inorganic and simple organic species that play a role in ozone formation, prioritizing the reactions that cause the most uncertainty in the modeling results. The updated mechanism is revision 5 of the Carbon Bond 6 mechanism, namely CB6r5. This report analyzes the impact of CB6r5 mechanism changes on air pollutant modeling in Texas.

2.0 DATA SOURCES FOR CB6R5

The types of chemical reaction data that are needed to develop gas-phase chemical mechanisms, such as CB6r5, include:

- Rate constants for thermal reactions, i.e., reactions that occur when atoms and/or molecules collide with each other in the atmosphere
- Absorption cross-sections and quantum yields for photolysis reactions, i.e., reactions that occur when molecules absorb sunlight and chemical bonds are broken
- Stoichiometric coefficients that define what products are formed and in what amount (yields) for thermal and photolysis reactions

Two panels of atmospheric scientists review chemical reaction data that are needed for atmospheric modeling:

- The International Union of Pure and Applied Chemistry (IUPAC) Task Group on Atmospheric Chemical Kinetic Data Evaluation. New reviews are produced continuously and are disseminated via http://iupac.pole-ether.fr/?cmd=redirect&arubalp=12345#. The recommended citation for this data (Atkinson et al., 2004) does not reflect the current panel membership or the currency of the data (i.e., more recent than 2004).
- The National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL) Panel for Data Evaluation. New reviews are produced periodically (most recently in 2015) and disseminated via http://jpldataeval.jpl.nasa.gov. The current evaluation is number 18 in the series and the citation is Burkholder et al., 2015.

These panels serve the important functions of:

- Identifying new information as it is published in the scientific literature
- Comparing new information to existing information
- Critically evaluating the body of scientific knowledge for each chemical reaction
- Providing recommendations for many, but not all, chemical reactions.

The products of both panels are quality assured and ready for use in chemical mechanisms such as CB6r5. The panels are independent and their recommendations for a specific chemical reaction may differ, but not by an amount that is greater than the uncertainty for that reaction.

CB6 mechanisms have generally relied more on recommendations from the IUPAC panel than the JPL panel, and this remains the case for CB6r5 updates. However, we consulted recommendations from both panels and relied on the JPL panel when there were specific reasons to do so, e.g., no recommendation from the IUPAC panel of a reaction included in CB6.

3.0 CB6 VERSION HISTORY

The first version of CB6 was completed in 2010 (Yarwood et al., 2010) using data available through mid-2010. The primary source for rate constant and photolysis data was the IUPAC panel (Atkinson et al., 2004 as updated through 2010) except that data from JPL evaluation number 15 (Sander et al., 2006) was used for NO_3 photolysis.

The first revision of CB6 to be widely used was CB6r2 (revision 2; Hildebrandt Ruiz and Yarwood, 2013) which was first released in CAMx in April 2014. CB6r2 introduced uptake of multi-functional organo-nitrates (ONs) by organic aerosol with subsequent hydrolysis to nitric acid. Also, the reaction mechanisms of isoprene and aromatics were updated from CB6.

CB6r2h added reactions of iodine, bromine and chlorine compounds to account for ozone destruction in the marine boundary layer of the Gulf of Mexico (Yarwood et al., 2014).

CB6r3 was developed to better represent wintertime high ozone events in the Rocky Mountains by accounting for temperature (and pressure) effects on alkyl nitrate formation (Emery et al., 2015). CB6r3 was designed to give similar ozone performance as CB6r2 for summer conditions.

CB6r4 was developed to model ozone depletion in the marine boundary layer more efficiently than CB6r2h. The halogen reactions included in CB6r2h noticeably slowed down CAMx simulations which was mitigated by developing a compact iodine mechanism (called I-16b) with just the 16 most important reactions of inorganic iodine (Emery et al., 2016). CB6r4 combined CB6r3 with the I-16b compact iodine mechanism.

CB6r4-DMS added reactions of dimethyl sulfide (DMS) to CB6r4 (Emery et al., 2019).

A listing of the CB6r4 mechanism in CAMx version 6.5 is shown in Appendix C of the User's Guide (Ramboll, 2018) available at http://www.camx.com/files/camxusersguide_v6-50.pdf. The same document explains the CB6r4 model species names and provides more details of photolysis reaction rates.

4.0 DEVELOPING CB6R5

4.1 Prioritizing Updates

Recently, Dunker et al. (2020) performed detailed sensitivity analysis of CB6r4 for conditions relevant to Texas ozone episodes and identified which mechanism parameters in CB6r4 make the largest contribution to uncertainty in ozone predictions. The "Top50" uncertain parameters in CB6r4 identified by Dunker et al. (2020) were given the highest priority for review and update (if needed) in CB6r5. In

addition, we reviewed most reactions involving nitrogen oxides (NOx), hydrogen oxide radicals (HOx) and odd oxygen radicals (Ox) regardless of whether they were in the Top50. Lastly, we reviewed the reactions of simpler organic compounds (methane, ethane, propane, ethene, ethyne, formaldehyde, acetaldehyde, acetone, benzene, toluene) with oxidants (OH, NO_3, O_3) and updated these reactions where possible.

4.2 Development Versions d1 to d3

CB6r5 development progressed through three development versions (d1 to d3) with CB6r5d3 being the final version. If development version isn't specified, then CB6r5 means CB6r5d3.

The first developmental version was named CB6r5d1. Testing of this version revealed widespread O_3 increases across Texas and elsewhere in the US that were associated with increased NO_2 in areas where O_3 production is NOx-limited. This finding prompted closer review of reaction updates that tended to increase the availability of NO_2 and consequently tend increase O_3 production. Two subsequent development versions further revised the rate constant for the OH + NO_2 reaction (ranked 8th in the Top50 most influential parameters; Dunker et al., 2020) and the reactions of PAN (ranked 2nd and 6th in the Top50) and PANX (ranked 4th and 9th in the Top50).

In CB6r5d1, the rate constant for the OH + NO_2 reaction was updated from the JPL recommendation to a newer IUPAC recommendation. New research from Amedro et al. (2020) provides new laboratory measurements for this reaction and analyzes the new data in conjunction with previously published studies (i.e., a similar analysis to those performed by JPL and NASA) and recommends a rate constant in between the recommendations of JPL and IUPAC. For CB6r5d2, we reverted the OH + NO_2 rate constant to the JPL recommendation (i.e., the same as CB6r4), deciding not to update this influential rate constant until there is more consensus among recommendations. The laboratory measurements of Amedro et al. (2020) also provide new insight by showing that water vapor accelerates the rate of the OH + NO_2 reaction (because H_2O is more effective as a third body, M, than either N_2 or O_2) which tends to accelerate the reaction in humid regions such as the boundary layer over the Gulf of Mexico and Texas. To account for this water effect, we analyzed the data of Amedro et al. (2020) and added the following reaction in CB6r5d2:

$$OH + NO_2 + H_2O = HNO_3 + H_2O \text{ with } k = 1.1E\text{-}30 \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}$$

CB6r5d3 modified CB6r5d2 by revising the reaction rate updates for peroxyacetyl nitrate (PAN) and related compounds (PANx and OPAN) that we implemented in CB6r5d1. The PAN formation reaction removes NO_2 but an opposing PAN dissociation reaction produces NO_2. As summarized in Table 1, the CB6r5d1 updates for PAN formation (5% decrease from CB6r4) and PAN dissociation (44% increase from CB6r4), from new IUPAC recommendations, amount to 49% reduction in PAN formation which tends to increase NO_2 and produce more O_3. The magnitude of this change (49%) was surprising and so we examined the discussion notes provided by IUPAC and JPL which were consistent in recommending almost identical equilibrium constant for PAN formation (2.26E-8 molecule cm^{-3} from IUPAC and 2.3E-8 molecule cm^{-3} from JPL). This equilibrium constant disagrees with the rate constants that IUPAC recommend (i.e., 2.07E-8 as shown in Table 2), and so for CB6r5d3 we adjusted the IUPAC rate constant for PAN formation (10% increase from CB6r5d1) to reproduce the recommended equilibrium constant (2.3E-8 molecule cm^{-3}). This adjustment moderates the amount of change in PAN reactions from CB6r4 to CB6r5d3. The formation and dissociation reactions of PANX were similarly adjusted in CB6r5d3 to have the same equilibrium constant as PAN and account for PANX dissociating faster than PAN. The rate constants for OPAN are set equal to PANX.

Table 1. Rate constants (k298) for formation and dissociation of PAN, PANX and OPAN in CB6r4, CB6r5d1 and CB6r5d3

No.	Reaction or Equilibrium Constant (K)	CB6r4	CB6r5d1	CB6r5d3
54	C2O3 + NO2 = PAN	9.40E-12	8.92E-12	9.86E-12
55	PAN = NO2 + C2O3	2.98E-04	4.31E-04	4.31E-04
	K_{PAN} = k54/k55	3.15E-08	2.07E-08	2.29E-08
62	CXO3 + NO2 = PANX	9.40E-12	7.37E-12	8.28E-12
63	PANX = NO2 + CXO3	2.98E-04	3.56E-04	3.62E-04
	K_{PANX}=k62/k63	3.15E-08	2.07E-08	2.29E-08
200	OPO3 + NO2 = OPAN	9.40E-12	7.37E-12	8.28E-12
201	OPAN = OPO3 + NO2	2.98E-04	3.56E-04	3.62E-04
	K_{OPAN}=k200/k201	3.15E-08	2.07E-08	2.29E-08

Notes:

(a) k_{298} is the rate constant at 298 K and 1 atmosphere using units in molecules/cm^3 and 1/s

(b) The equilibrium constant (K) is defined as the ratio of formation/dissociation rate constants

5.0 THE CB6R5 MECHANISM

A complete listing of the updated CB6r5 mechanism (i.e., CB6r5d3) is shown in Table 2 with changes from CB6r4 shown in red (additions) and strikeout (deletions). A summary of the changes is:

- 152 reactions were reviewed for the update from CB6r4 to CB6r5 according to the priorities discussed above
- CB6r5 has one more reaction than CB6r4 (reaction 234 is new)
- 47 reaction rates are changed in CB6r5 from CB6r4 because newer data are available
- 41 of 47 changes are for rate constants and there are new CAMx chemistry parameter input files for CB6r5
- 6 of 47 changes are for photolysis reactions, for FORM (2 reactions), ALD2, ALDX, GLY and GLYD, and there is an updated TUV photolysis rate model for CB6r5 in CAMx
- The largest reaction rate increase (CB6r5/CB6r4 = 9.1) is for GLY photolysis
- The largest reaction rate decrease (CB6r5/CB6r4 = 0.15) is for NO3 + GLY
- CB6r5 and CB6r4 have identical chemical species; no changes are needed to CAMx inputs (emissions, boundary conditions) for CB6r5 from CB6r4.

The 152 reactions that were reviewed for CB6r5 are listed in Table 3 along with ratios of rate constants in CB6r5 to CB6r4 and the data sources used for each rate constant update.

In addition to rate constant updates, there were several changes to reaction products for CB6r5:

- For reaction 4 (O + NO), IUPAC revised how pressure is accounted for by changing from a 3rd order reaction (M included as a reactant) to a 2nd order reaction with a rate constant that depends on M (i.e., a Troe expression, explained in the CAMx User's Guide)
- For reaction 57 (C2O3 + HO2), IUPAC changed the OH yield from 44% to 50% which changed other product yields, and caused corresponding changes in reactions 65 (CXO3 + HO2) and 202 (OPO3 + HO2)

- We corrected errors in products of reactions 58, 66 and 67.

Table 2. The CB6r5 mechanism with changes from CB6r4 marked.

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
1	NO2 = NO + O	Photolysis	6.30E-3
2	O + O2 + M = O3 + M	k = ~~5.68E~~6.00E-34 (T/300)^-2.6	~~5.78E~~6.11E-34
3	O3 + NO = NO2	k = ~~1.40E~~2.07E-12 exp(-~~1310~~1400/T)	1.~~73E~~89E-14
4	O + NO ~~+ M~~ = NO2 ~~+ M~~	Falloff: F=0.85; n=0.84 k(0) = 1.00E-31 (T/300)^-1.6 k(inf) = 5.00E-11 (T/300)^-0.3	~~1.01E-31~~2.26E-12
5	O + NO2 = NO	k = 5.~~50E~~10E-12 exp(~~188~~198/T)	~~1.03E-11~~9.91E-12
6	O + NO2 = NO3	Falloff: F=0.6; n=1.03 k(0) = 1.30E-31 (T/300)^-1.5 k(inf) = 2.30E-11 (T/300)^0.24	2.~~11E~~09E-12
7	O + O3 =	k = 8.00E-12 exp(-2060/T)	7.96E-15
8	O3 = O	Photolysis	3.33E-4
9	O3 = O1D	Photolysis	8.78E-6
10	O1D + M = O + M	k = 2.23E-11 exp(115/T)	3.28E-11
11	O1D + H2O = 2 OH	k = 2.14E-10	2.14E-10
12	O3 + OH = HO2	k = 1.70E-12 exp(-940/T)	7.25E-14
13	O3 + HO2 = OH	k = 2.03E-16 (T/300)^4.57 exp(693/T)	2.01E-15
14	OH + O = HO2	k = 2.40E-11 exp(110/T)	3.47E-11
15	HO2 + O = OH	k = ~~2.70E~~3.00E-11 exp(~~224~~200/T)	5.~~73E~~87E-11
16	OH + OH = O	k = 6.20E-14 (T/298)^2.6 exp(945/T)	1.48E-12
17	OH + OH = H2O2	Falloff: F=0.~~5~~42; n=1.~~13~~23 k(0) = ~~6.90E~~9.00E-31 (T/300)^-~~0.8~~3.2 k(inf) = ~~2.60E~~3.90E-11 (T/300)^-0.47	~~5.25E~~6.21E-12
18	OH + HO2 =	k = 4.80E-11 exp(250/T)	1.11E-10
19	HO2 + HO2 = H2O2	k = k1 + k2 [M] k1 = 2.20E-13 exp(600/T) k2 = 1.90E-33 exp(980/T)	2.90E-12
20	HO2 + HO2 + H2O = H2O2	k = k1 + k2 [M] k1 = 3.08E-34 exp(2800/T) k2 = 2.66E-54 exp(3180/T)	6.53E-30
21	H2O2 = 2 OH	Photolysis	3.78E-6
22	H2O2 + OH = HO2	k = ~~2.90E~~1.80E-12 ~~exp(160/T)~~	1.~~70E~~80E-12
23	H2O2 + O = OH + HO2	k = 1.40E-12 exp(-2000/T)	1.70E-15
24	NO + NO + O2 = 2 NO2	k = ~~3.30E~~4.25E-39 exp(~~530~~664/T)	~~1~~3.95E-38
25	HO2 + NO = OH + NO2	k = 3.45E-12 exp(270/T)	8.54E-12
26	NO2 + O3 = NO3	k = 1.40E-13 exp(-2470/T)	3.52E-17

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
27	NO3 = NO2 + O	Photolysis	1.56E-1
28	NO3 = NO	Photolysis	1.98E-2
29	NO3 + NO = 2 NO2	k = 1.80E-11 exp(110/T)	2.60E-11
30	NO3 + NO2 = NO + NO2	k = 4.50E-14 exp(-1260/T)	6.56E-16
31	NO3 + O = NO2	k = 1.70E-11	1.70E-11
32	NO3 + OH = HO2 + NO2	k = 2.00E-11	2.00E-11
33	NO3 + HO2 = OH + NO2	k = 4.00E-12	4.00E-12
34	NO3 + O3 = NO2	k = 1.00E-17	1.00E-17
35	NO3 + NO3 = 2 NO2	k = 8.50E-13 exp(-2450/T)	2.28E-16
36	NO3 + NO2 = N2O5	Falloff: F=0.35; n=1.33 k(0) = 3.60E-30 (T/300)^-4.1 k(inf) = 1.90E-12 (T/300)^0.2	1.24E-12
37	N2O5 = NO3 + NO2	Falloff: F=0.35; n=1.33 k(0) = 1.30E-3 (T/300)^-3.5 exp(-11000/T) k(inf) = 9.70E+14 (T/300)^0.1 exp(-11080/T)	4.46E-2
38	N2O5 = NO2 + NO3	Photolysis	2.52E-5
39	N2O5 + H2O = 2 HNO3	k = 1.00E-22	1.00E-22
40	NO + OH = HONO	Falloff: F=0.81; n=0.87 k(0) = 7.40E-31 (T/300)^-2.4 k(inf) = 3.30E-11 (T/300)^-0.3	9.77E-12
41	NO + NO2 + H2O = 2 HONO	k = 5.00E-40	5.00E-40
42	HONO + HONO = NO + NO2	k = 1.00E-20	1.00E-20
43	HONO = NO + OH	Photolysis	1.04E-3
44	HONO + OH = NO2	k = 2.50E-12 exp(260/T)	5.98E-12
45	NO2 + OH = HNO3	Falloff: F=0.6; n=1 k(0) = 1.80E-30 (T/300)^-3 k(inf) = 2.80E-11	1.06E-11
46	HNO3 + OH = NO3	k = k1 + k3 [M] / (1 + k3 [M] / k2) k1 = 2.40E-14 exp(460/T) k2 = 2.70E-17 exp(2199/T) k3 = 6.50E-34 exp(1335/T)	1.54E-13
47	HNO3 = OH + NO2	Photolysis	2.54E-7
48	HO2 + NO2 = PNA	Falloff: F=0.~~64~~; n=1.26 k(0) = 1.~~80E~~40E-31 (T/300)^-3.~~2~~1 k(inf) = 4.~~70E~~00E-12	~~1.38E-12~~7.50E-13
49	PNA = HO2 + NO2	Falloff: F=0.~~64~~; n=1.26 k(0) = 4.10E-5 exp(-10650/T) k(inf) = ~~4.80E~~6.00E+15 exp(-11170/T)	~~8.31E~~6.20E-2
50	PNA = 0.59 HO2 + 0.59 NO2 + 0.41 OH + 0.41 NO3	Photolysis	2.36E-6

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
51	PNA + OH = NO2	k = 3.20E-13 exp(690/T)	3.24E-12
52	SO2 + OH = SULF + HO2	Falloff: F=0.53; n=1.1 k(0) = ~~4.50E~~2.80E-31 (T/300)^-~~3.92~~.6 k(inf) = ~~1.30E~~2.00E-12~~ (T/300)^ 0.7~~	~~8.12E~~9.35E-13
53	C2O3 + NO = NO2 + MEO2 + RO2	k = 7.50E-12 exp(290/T)	1.98E-11
54	C2O3 + NO2 = PAN	Falloff: F=0.3; n=1.41 k(0) = ~~2.70E~~3.61E-28 (T/300)^-~~7.1~~6.87 k(inf) = 1.~~20E~~24E-11 (T/300)^-~~0.9~~1.105	9.~~40E~~86E-12
55	PAN = NO2 + C2O3	Falloff: F=0.3; n=1.41 k(0) = ~~4.90E-3~~1.10E-5 exp(-~~12100~~10100/T) k(inf) = ~~5.40E+16~~1.90E+17 exp(-~~13830~~14100/T)	~~2.98E~~4.31E-4
56	PAN = 0.6 NO2 + 0.6 C2O3 + 0.4 NO3 + 0.4 MEO2 + 0.4 RO2	Photolysis	3.47E-7
57	C2O3 + HO2 = 0.~~41~~37 PACD + 0.~~15~~13 AACD + 0.~~15~~13 O3 + 0.~~44~~5 OH + 0.5 MEO2 + 0.~~44~~5 RO2~~ + 0.44 OH~~	k = ~~5.20E-13~~3.14E-12 exp(~~980~~580/T)	~~1.39E~~2.20E-11
58	C2O3 + RO2 = ~~C2O3~~MEO2	k = ~~8.90E~~4.40E-13 exp(~~800~~1070/T)	1.~~30E~~60E-11
59	C2O3 + C2O3 = 2 MEO2 + 2 RO2	k = 2.90E-12 exp(500/T)	1.55E-11
60	C2O3 + CXO3 = MEO2 + ALD2 + XO2H + 2 RO2	~~k = 2.90E-12 exp(500/T)~~k = k(ref)/K k(ref) = k(59) K = 1.00E+0	1.55E-11
61	CXO3 + NO = NO2 + ALD2 + XO2H + RO2	k = 6.70E-12 exp(340/T)	2.10E-11
62	CXO3 + NO2 = PANX	k = k(ref)/K k(ref) = k(54) K = 1.~~00E~~19E+0	~~9.40E~~8.28E-12
63	PANX = NO2 + CXO3	k = k(ref)/K k(ref) = k(55) K = 1.~~00E~~19E+0	~~2.98E~~3.62E-4
64	PANX = 0.6 NO2 + 0.6 CXO3 + 0.4 NO3 + 0.4 ALD2 + 0.4 XO2H + 0.4 RO2	Photolysis	3.47E-7
65	CXO3 + HO2 = 0.~~41~~37 PACD + 0.~~15~~13 AACD + 0.~~15~~13 O3 + 0.~~44 ALD2~~5 OH + 0.~~44 XO2H~~5 MEO2 + 0.~~44~~5 RO2~~ + 0.44 OH~~	~~k = 5.20E-13 exp(980/T)~~k = k(ref)/K k(ref) = k(57) K = 1.00E+0	~~1.39E~~2.20E-11
66	CXO3 + RO2 = ~~0.8 ALD2 + 0.8 XO2H + 0.8 RO2~~MEO2	~~k = 8.90E-13 exp(800/T)~~k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
67	CXO3 + CXO3 = 2 ~~ALD2 + 2 XO2H~~MEO2 + 2 RO2	~~k = 3.20E-12 exp(500/T)~~k = k(ref)/K k(ref) = k(59) K = 1.00E+0	1.~~71E~~55E-11

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
68	RO2 + NO = NO	k = 2.40E-12 exp(360/T)	8.03E-12
69	RO2 + HO2 = HO2	k = 4.80E-13 exp(800/T)	7.03E-12
70	RO2 + RO2 =	k = 6.50E-14 exp(500/T)	3.48E-13
71	MEO2 + NO = FORM + HO2 + NO2	k = 2.30E-12 exp(360/T)	7.70E-12
72	MEO2 + HO2 = 0.9 MEPX + 0.1 FORM	k = 3.80E-13 exp(780/T)	5.21E-12
73	MEO2 + C2O3 = FORM + 0.9 HO2 + 0.9 MEO2 + 0.1 AACD + 0.9 RO2	k = 2.00E-12 exp(500/T)	1.07E-11
74	MEO2 + RO2 = 0.685 FORM + 0.315 MEOH + 0.37 HO2 + RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
75	XO2H + NO = NO2 + HO2	k = 2.70E-12 exp(360/T)	9.04E-12
76	XO2H + HO2 = ROOH	k = 6.80E-13 exp(800/T)	9.96E-12
77	XO2H + C2O3 = 0.8 HO2 + 0.8 MEO2 + 0.2 AACD + 0.8 RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
78	XO2H + RO2 = 0.6 HO2 + RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
79	XO2 + NO = NO2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12
80	XO2 + HO2 = ROOH	k = k(ref)/K k(ref) = k(76) K = 1.00E+0	9.96E-12
81	XO2 + C2O3 = 0.8 MEO2 + 0.2 AACD + 0.8 RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
82	XO2 + RO2 = RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
83	XO2N + NO = 0.5 NTR1 + 0.5 NTR2	k = k(ref)/K k(ref) = k(75) K = 1.00E+0	9.04E-12
84	XO2N + HO2 = ROOH	k = k(ref)/K k(ref) = k(76) K = 1.00E+0	9.96E-12
85	XO2N + C2O3 = 0.8 HO2 + 0.8 MEO2 + 0.2 AACD + 0.8 RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
86	XO2N + RO2 = RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
87	MEPX + OH = 0.6 MEO2 + 0.6 RO2 + 0.4 FORM + 0.4 OH	k = 5.30E-12 exp(190/T)	1.00E-11

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
88	MEPX = MEO2 + RO2 + OH	Photolysis	2.68E-6
89	ROOH + OH = 0.54 XO2H + 0.06 XO2N + 0.6 RO2 + 0.4 OH	k = 5.30E-12 exp(190/T)	1.00E-11
90	ROOH = HO2 + OH	Photolysis	2.68E-6
91	NTR1 + OH = NTR2	k = 2.00E-12	2.00E-12
92	NTR1 = NO2	Photolysis	1.06E-6
93	FACD + OH = HO2	k = 4.50E-13	4.50E-13
94	AACD + OH = MEO2 + RO2	k = 4.00E-14 exp(850/T)	6.93E-13
95	PACD + OH = C2O3	k = 5.30E-12 exp(190/T)	1.00E-11
96	FORM + OH = HO2 + CO	k = 5.40E-12 exp(135/T)	8.49E-12
97	FORM = 2 HO2 + CO	Photolysis	1.~~78E~~69E-5
98	FORM = CO + H2	Photolysis	2.~~38E~~69E-5
99	FORM + NO3 = HNO3 + HO2 + CO	k = 5.50E-16	5.50E-16
100	FORM + HO2 = HCO3	k = 9.70E-15 exp(625/T)	7.90E-14
101	HCO3 = FORM + HO2	k = 2.40E+12 exp(-7000/T)	1.51E+2
102	HCO3 + NO = FACD + NO2 + HO2	k = 5.60E-12	5.60E-12
103	HCO3 + HO2 = 0.5 MEPX + 0.5 FACD + 0.2 OH + 0.2 HO2	k = 5.60E-15 exp(2300/T)	1.26E-11
104	ALD2 + OH = C2O3	k = 4.70E-12 exp(345/T)	1.50E-11
105	ALD2 + NO3 = C2O3 + HNO3	k = 1.40E-12 exp(-1860/T)	2.73E-15
106	ALD2 = MEO2 + RO2 + CO + HO2	Photolysis	1.~~76E~~96E-6
107	ALDX + OH = CXO3	k = 4.90E-12 exp(405/T)	1.91E-11
108	ALDX + NO3 = CXO3 + HNO3	k = 6.30E-15	6.30E-15
109	ALDX = ALD2 + XO2H + RO2 + CO + HO2	Photolysis	~~6.96E-6~~2.62E-5
110	GLYD + OH = 0.2 GLY + 0.2 HO2 + 0.8 C2O3	k = 8.00E-12	8.00E-12
111	GLYD = 0.74 FORM + 0.89 CO + 1.4 HO2 + 0.15 MEOH + 0.19 OH + 0.11 GLY + 0.11 XO2H + 0.11 RO2	Photolysis	~~1.56E~~2.76E-6
112	GLYD + NO3 = HNO3 + C2O3	k = k(ref)/K k(ref) = k(105) K = 1.~~40E-12 exp(-1860/T)~~00E+0	2.73E-15
113	GLY + OH = 1.8 CO + 0.2 XO2 + 0.2 RO2 + HO2	k = 3.10E-12 exp(340/T)	9.70E-12
114	GLY = 2 HO2 + 2 CO	Photolysis	5.~~50E-5~~01E-4
115	GLY + NO3 = HNO3 + 1.5 CO + 0.5 XO2 + 0.5 RO2 + HO2	k = ~~1.40E-12 exp(-1860/T)~~4.00E-16	~~2.73E-15~~4.00E-16
116	MGLY = C2O3 + HO2 + CO	Photolysis	1.46E-4
117	MGLY + NO3 = HNO3 + C2O3 + XO2 + RO2	k = ~~1.40E-12 exp(-1860/T)~~5.00E-16	~~2.73E-15~~5.00E-16
118	MGLY + OH = C2O3 + CO	k = 1.90E-12 exp(575/T)	1.31E-11

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
119	H2 + OH = HO2	k = 7.70E-12 exp(-2100/T)	6.70E-15
120	CO + OH = HO2	k = k1 + k2 [M] k1 = 1.44E-13 k2 = 3.43E-33	2.28E-13
121	CH4 + OH = MEO2 + RO2	k = 1.85E-12 exp(-1690/T)	6.37E-15
122	ETHA + OH = 0.991 ALD2 + 0.991 XO2H + 0.009 XO2N + RO2	k = 6.90E-12 exp(-1000/T)	2.41E-13
123	MEOH + OH = FORM + HO2	k = 2.85E-12 exp(-345/T)	8.95E-13
124	ETOH + OH = 0.95 ALD2 + 0.9 HO2 + 0.1 XO2H + 0.1 RO2 + 0.078 FORM + 0.011 GLYD	k = 3.00E-12 exp(20/T)	3.21E-12
125	KET = 0.5 ALD2 + 0.5 C2O3 + 0.5 XO2H + 0.5 CXO3 + 0.5 MEO2 + RO2 - 2.5 PAR	Photolysis	2.27E-7
126	ACET = 0.38 CO + 1.38 MEO2 + 1.38 RO2 + 0.62 C2O3	Photolysis	2.08E-7
127	ACET + OH = FORM + C2O3 + XO2 + RO2	k = 1.41E-12 exp(-620.6/T)	1.76E-13
128	PRPA + OH = XPRP	k = 7.60E-12 exp(-585/T)	1.07E-12
129	PAR + OH = XPAR	k = 8.10E-13	8.10E-13
130	ROR = 0.2 KET + 0.42 ACET + 0.74 ALD2 + 0.37 ALDX + 0.04 XO2N + 0.94 XO2H + 0.98 RO2 + 0.02 ROR - 2.7 PAR	k = 5.70E+12 exp(-5780/T)	2.15E+4
131	ROR + O2 = KET + HO2	k = 1.50E-14 exp(-200/T)	7.67E-15
132	ROR + NO2 = NTR1	k = 8.60E-12 exp(400/T)	3.29E-11
133	ETHY + OH = 0.7 GLY + 0.7 OH + 0.3 FACD + 0.3 CO + 0.3 HO2	Falloff: F=0.37; n=1.3 k(0) = 5.00E-30 (T/300)^-1.5 k(inf) = 1.00E-12	7.52E-13
134	ETH + OH = XO2H + RO2 + 1.56 FORM + 0.22 GLYD	Falloff: F=0.48; n=1.15 k(0) = 8.60E-29 (T/300)^-3.1 k(inf) = 9.00E-12 (T/300)^-0.85	7.84E-12
135	ETH + O3 = FORM + 0.~~51~~35 CO + 0.~~16~~27 HO2 + 0.~~16~~17 OH + 0.~~37~~42 FACD	k = ~~9.10E~~6.82E-15 exp(-~~2580~~2500/T)	1.~~58E~~55E-18
136	ETH + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.5 XO2H + 0.5 XO2 + RO2 + 1.125 FORM	k = 3.30E-12 exp(-2880/T)	2.10E-16
137	OLE + OH = 0.781 FORM + 0.488 ALD2 + 0.488 ALDX + 0.976 XO2H + 0.195 XO2 + 0.024 XO2N + 1.195 RO2 - 0.73 PAR	Falloff: F=0.5; n=1.13 k(0) = 8.00E-27 (T/300)^-3.5 k(inf) = 3.00E-11 (T/300)^-1	2.86E-11
138	OLE + O3 = 0.295 ALD2 + 0.555 FORM + 0.27 ALDX + 0.15 XO2H + 0.15 RO2 + 0.334 OH + 0.08 HO2 + 0.378 CO + 0.075 GLY + 0.075 MGLY + 0.09 FACD + 0.13 AACD + 0.04 H2O2 - 0.79 PAR	k = 5.50E-15 exp(-1880/T)	1.00E-17

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
139	OLE + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.48 XO2 + 0.48 XO2H + 0.04 XO2N + RO2 + 0.5 FORM + 0.25 ALD2 + 0.375 ALDX - 1 PAR	k = 4.60E-13 exp(-1155/T)	9.54E-15
140	IOLE + OH = 1.3 ALD2 + 0.7 ALDX + XO2H + RO2	k = 1.05E-11 exp(519/T)	5.99E-11
141	IOLE + O3 = 0.732 ALD2 + 0.442 ALDX + 0.128 FORM + 0.245 CO + 0.5 OH + 0.3 XO2H + 0.3 RO2 + 0.24 GLY + 0.06 MGLY + 0.29 PAR + 0.08 AACD + 0.08 H2O2	k = 4.70E-15 exp(-1013/T)	1.57E-16
142	IOLE + NO3 = 0.5 NO2 + 0.5 NTR1 + 0.48 XO2 + 0.48 XO2H + 0.04 XO2N + RO2 + 0.5 ALD2 + 0.625 ALDX + PAR	k = 3.70E-13	3.70E-13
143	ISOP + OH = ISO2 + RO2	k = 2.70E-11 exp(390/T)	9.99E-11
144	ISO2 + NO = 0.1 INTR + 0.9 NO2 + 0.673 FORM + 0.9 ISPD + 0.818 HO2 + 0.082 XO2H + 0.082 RO2	k = 2.39E-12 exp(365/T)	8.13E-12
145	ISO2 + HO2 = 0.88 ISPX + 0.12 OH + 0.12 HO2 + 0.12 FORM + 0.12 ISPD	k = 7.43E-13 exp(700/T)	7.78E-12
146	ISO2 + C2O3 = 0.598 FORM + 1 ISPD + 0.728 HO2 + 0.072 XO2H + 0.8 MEO2 + 0.2 AACD + 0.872 RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
147	ISO2 + RO2 = 0.598 FORM + 1 ISPD + 0.728 HO2 + 0.072 XO2H + 1.072 RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
148	ISO2 = HO2 + HPLD	k = 3.30E+9 exp(-8300/T)	2.64E-3
149	ISOP + O3 = 0.6 FORM + 0.65 ISPD + 0.15 ALDX + 0.2 CXO3 + 0.35 PAR + 0.266 OH + 0.2 XO2 + 0.2 RO2 + 0.066 HO2 + 0.066 CO	k = 1.03E-14 exp(-1995/T)	1.27E-17
150	ISOP + NO3 = 0.35 NO2 + 0.65 NTR2 + 0.64 XO2H + 0.33 XO2 + 0.03 XO2N + RO2 + 0.35 FORM + 0.35 ISPD	k = 3.03E-12 exp(-448/T)	6.74E-13
151	ISPD + OH = 0.022 XO2N + 0.521 XO2 + 0.115 MGLY + 0.115 MEO2 + 0.269 GLYD + 0.269 C2O3 + 0.457 OPO3 + 0.117 PAR + 0.137 ACET + 0.137 CO + 0.137 HO2 + 0.658 RO2	k = 5.58E-12 exp(511/T)	3.10E-11
152	ISPD + O3 = 0.04 ALD2 + 0.231 FORM + 0.531 MGLY + 0.17 GLY + 0.17 ACET + 0.543 CO + 0.461 OH + 0.15 FACD + 0.398 HO2 + 0.143 C2O3	k = 3.88E-15 exp(-1770/T)	1.02E-17
153	ISPD + NO3 = 0.717 HNO3 + 0.142 NTR2 + 0.142 NO2 + 0.142 XO2 + 0.142 XO2H + 0.113 GLYD + 0.113 MGLY + 0.717 PAR + 0.717 CXO3 + 0.284 RO2	k = 4.10E-12 exp(-1860/T)	7.98E-15

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
154	ISPD = 0.76 HO2 + 0.34 XO2H + 0.16 XO2 + 0.34 MEO2 + 0.208 C2O3 + 0.26 FORM + 0.24 OLE + 0.24 PAR + 0.17 ACET + 0.128 GLYD + 0.84 RO2	Photolysis	1.60E-5
155	ISPX + OH = 0.904 EPOX + 0.933 OH + 0.067 ISO2 + 0.067 RO2 + 0.029 IOLE + 0.029 ALDX	k = 2.23E-11 exp(372/T)	7.77E-11
156	HPLD = OH + ISPD	Photolysis	4.41E-4
157	HPLD + NO3 = HNO3 + ISPD	k = 6.00E-12 exp(-1860/T)	1.17E-14
158	EPOX + OH = EPX2 + RO2	k = 5.78E-11 exp(-400/T)	1.51E-11
159	EPX2 + HO2 = 0.275 GLYD + 0.275 GLY + 0.275 MGLY + 1.125 OH + 0.825 HO2 + 0.375 FORM + 0.074 FACD + 0.251 CO + 2.175 PAR	k = 7.43E-13 exp(700/T)	7.78E-12
160	EPX2 + NO = 0.275 GLYD + 0.275 GLY + 0.275 MGLY + 0.125 OH + 0.825 HO2 + 0.375 FORM + NO2 + 0.251 CO + 2.175 PAR	k = 2.39E-12 exp(365/T)	8.13E-12
161	EPX2 + C2O3 = 0.22 GLYD + 0.22 GLY + 0.22 MGLY + 0.1 OH + 0.66 HO2 + 0.3 FORM + 0.2 CO + 1.74 PAR + 0.8 MEO2 + 0.2 AACD + 0.8 RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
162	EPX2 + RO2 = 0.275 GLYD + 0.275 GLY + 0.275 MGLY + 0.125 OH + 0.825 HO2 + 0.375 FORM + 0.251 CO + 2.175 PAR + RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
163	INTR + OH = 0.63 XO2 + 0.37 XO2H + RO2 + 0.444 NO2 + 0.185 NO3 + 0.104 INTR + 0.592 FORM + 0.331 GLYD + 0.185 FACD + 2.7 PAR + 0.098 OLE + 0.078 ALDX + 0.266 NTR2	k = 3.10E-11	3.10E-11
164	TERP + OH = 0.75 XO2H + 0.5 XO2 + 0.25 XO2N + 1.5 RO2 + 0.28 FORM + 1.66 PAR + 0.47 ALDX	k = 1.50E-11 exp(449/T)	6.77E-11
165	TERP + O3 = 0.57 OH + 0.07 XO2H + 0.69 XO2 + 0.18 XO2N + 0.94 RO2 + 0.24 FORM + 0.001 CO + 7 PAR + 0.21 ALDX + 0.39 CXO3	k = 1.20E-15 exp(-821/T)	7.63E-17
166	TERP + NO3 = 0.47 NO2 + 0.28 XO2H + 0.75 XO2 + 0.25 XO2N + 1.28 RO2 + 0.47 ALDX + 0.53 NTR2	k = 3.70E-12 exp(175/T)	6.66E-12
167	BENZ + OH = 0.53 CRES + 0.352 BZO2 + 0.352 RO2 + 0.118 OPEN + 0.118 OH + 0.53 HO2	k = 2.30E-12 exp(-190/T)	1.22E-12
168	BZO2 + NO = 0.918 NO2 + 0.082 NTR2 + 0.918 GLY + 0.918 OPEN + 0.918 HO2	k = 2.70E-12 exp(360/T)	9.04E-12

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
169	BZO2 + C2O3 = GLY + OPEN + HO2 + MEO2 + RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
170	BZO2 + HO2 =	k = 1.90E-13 exp(1300/T)	1.49E-11
171	BZO2 + RO2 = GLY + OPEN + HO2 + RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
172	TOL + OH = 0.18 CRES + 0.65 TO2 + 0.72 RO2 + 0.1 OPEN + 0.1 OH + 0.07 XO2H + 0.18 HO2	k = 1.80E-12 exp(340/T)	5.63E-12
173	TO2 + NO = 0.86 NO2 + 0.14 NTR2 + 0.417 GLY + 0.443 MGLY + 0.66 OPEN + 0.2 XOPN + 0.86 HO2	k = 2.70E-12 exp(360/T)	9.04E-12
174	TO2 + C2O3 = 0.48 GLY + 0.52 MGLY + 0.77 OPEN + 0.23 XOPN + HO2 + MEO2 + RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
175	TO2 + HO2 =	k = 1.90E-13 exp(1300/T)	1.49E-11
176	TO2 + RO2 = 0.48 GLY + 0.52 MGLY + 0.77 OPEN + 0.23 XOPN + HO2 + RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
177	XYL + OH = 0.155 CRES + 0.544 XLO2 + 0.602 RO2 + 0.244 XOPN + 0.244 OH + 0.058 XO2H + 0.155 HO2	k = 1.85E-11	1.85E-11
178	XLO2 + NO = 0.86 NO2 + 0.14 NTR2 + 0.221 GLY + 0.675 MGLY + 0.3 OPEN + 0.56 XOPN + 0.86 HO2	k = 2.70E-12 exp(360/T)	9.04E-12
179	XLO2 + HO2 =	k = 1.90E-13 exp(1300/T)	1.49E-11
180	XLO2 + C2O3 = 0.26 GLY + 0.77 MGLY + 0.35 OPEN + 0.65 XOPN + HO2 + MEO2 + RO2	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
181	XLO2 + RO2 = 0.26 GLY + 0.77 MGLY + 0.35 OPEN + 0.65 XOPN + HO2 + RO2	k = k(ref)/K k(ref) = k(70) K = 1.00E+0	3.48E-13
182	CRES + OH = 0.025 GLY + 0.025 OPEN + HO2 + 0.2 CRO + 0.732 CAT1 + 0.02 XO2N + 0.02 RO2	k = 1.70E-12 exp(950/T)	4.12E-11
183	CRES + NO3 = 0.3 CRO + HNO3 + 0.48 XO2 + 0.12 XO2H + 0.24 GLY + 0.24 MGLY + 0.48 OPO3 + 0.1 XO2N + 0.7 RO2	k = 1.40E-11	1.40E-11
184	CRO + NO2 = CRON	k = 2.10E-12	2.10E-12
185	CRO + HO2 = CRES	k = 5.50E-12	5.50E-12
186	CRON + OH = NTR2 + 0.5 CRO	k = 1.53E-12	1.53E-12
187	CRON + NO3 = NTR2 + 0.5 CRO + HNO3	k = 3.80E-12	3.80E-12

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
188	CRON = HONO + HO2 + FORM + OPEN	Photolysis	9.45E-5
189	XOPN = 0.4 GLY + XO2H + 0.7 HO2 + 0.7 CO + 0.3 C2O3	Photolysis	5.04E-4
190	XOPN + OH = MGLY + 0.4 GLY + 2 XO2H + 2 RO2	k = 9.00E-11	9.00E-11
191	XOPN + O3 = 1.2 MGLY + 0.5 OH + 0.6 C2O3 + 0.1 ALD2 + 0.5 CO + 0.3 XO2H + 0.3 RO2	k = 1.08E-16 exp(-500/T)	2.02E-17
192	XOPN + NO3 = 0.5 NO2 + 0.5 NTR2 + 0.45 XO2H + 0.45 XO2 + 0.1 XO2N + RO2 + 0.25 OPEN + 0.25 MGLY	k = 3.00E-12	3.00E-12
193	OPEN = OPO3 + HO2 + CO	Photolysis	5.04E-4
194	OPEN + OH = 0.6 OPO3 + 0.4 XO2H + 0.4 RO2 + 0.4 GLY	k = 4.40E-11	4.40E-11
195	OPEN + O3 = 1.4 GLY + 0.24 MGLY + 0.5 OH + 0.12 C2O3 + 0.08 FORM + 0.02 ALD2 + 1.98 CO + 0.56 HO2	k = 5.40E-17 exp(-500/T)	1.01E-17
196	OPEN + NO3 = OPO3 + HNO3	k = 3.80E-12	3.80E-12
197	CAT1 + OH = 0.14 FORM + 0.2 HO2 + 0.5 CRO	k = 5.00E-11	5.00E-11
198	CAT1 + NO3 = CRO + HNO3	k = 1.70E-10	1.70E-10
199	OPO3 + NO = NO2 + 0.5 GLY + 0.5 CO + 0.8 HO2 + 0.2 CXO3	k = k(ref)/K k(ref) = k(61) K = 1.00E~~-11~~+0	~~1.00E~~2.10E-11
200	OPO3 + NO2 = OPAN	k = k(ref)/K k(ref) = k(~~54~~62) K = 1.00E+0	~~9.40E~~8.28E-12
201	OPAN = OPO3 + NO2	k = k(ref)/K k(ref) = k(~~55~~63) K = 1.00E+0	~~2.98E~~3.62E-4
202	OPO3 + HO2 = 0.~~41~~37 PACD + 0.~~15~~13 AACD + 0.~~15~~13 O3 + 0.~~44 ALDX~~5 OH + 0.~~44 XO2H~~5 MEO2 + 0.~~44~~5 RO2~~ + 0.44 OH~~	k = k(ref)/K k(ref) = k(57) K = 1.00E+0	~~1.39E~~2.20E-11
203	OPO3 + C2O3 = MEO2 + XO2 + ALDX + 2 RO2	k = k(ref)/K k(ref) = k(59) K = 1.00E+0	1.55E-11
204	OPO3 + RO2 = 0.8 XO2H + 0.8 ALDX + 1.8 RO2 + 0.2 AACD	k = k(ref)/K k(ref) = k(58) K = 1.00E+0	1.~~30E~~60E-11
205	OPAN + OH = 0.5 NO2 + 0.5 GLY + CO + 0.5 NTR2	k = 3.60E-11	3.60E-11
206	PANX + OH = ALD2 + NO2	k = 3.00E-12	3.00E-12
207	NTR2 = HNO3	k = 2.30E-5	2.30E-5

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
208	ECH4 + OH = MEO2 + RO2	k = 1.85E-12 exp(-1690/T)	6.37E-15
209	I2 = 2 I	Photolysis	1.44E-1
210	HOI = I + OH	Photolysis	6.36E-2
211	I + O3 = IO	k = 2.10E-11 exp(-830/T)	1.30E-12
212	IO = I + O	Photolysis	1.18E-1
213	IO + IO = 0.4 I + 0.4 OIO + 0.6 I2O2	k = 5.40E-11 exp(180/T)	9.88E-11
214	IO + HO2 = HOI	k = 1.40E-11 exp(540/T)	8.57E-11
215	IO + NO = I + NO2	k = 7.15E-12 exp(300/T)	1.96E-11
216	IO + NO2 = INO3	Falloff: F=0.4; n=1.26 k(0) = 7.70E-31 (T/300)^-5 k(inf) = 1.60E-11	3.~~55E~~54E-12
217	OIO = I	Photolysis	1.41E-1
218	OIO + OH = HIO3	Falloff: F=0.3; n=1.41 k(0) = 1.50E-27 (T/300)^-3.93 k(inf) = 5.50E-10 exp(46/T)	~~4.72E~~3.96E-10
219	OIO + IO = IXOY	k = 1.00E-10	1.00E-10
220	OIO + NO = IO + NO2	k = 1.10E-12 exp(542/T)	6.78E-12
221	I2O2 = I + OIO	k = 1.00E+1	1.00E+1
222	I2O2 + O3 = IXOY	k = 1.00E-12	1.00E-12
223	INO3 = I + NO3	Photolysis	1.25E-2
224	INO3 + H2O = HOI + HNO3	k = 2.50E-22	2.50E-22
225	XPRP = XO2N + RO2	Falloff: F=0.41; n=1 k(0) = 2.37E-21 k(inf) = 4.30E-1 (T/298)^-8	3.09E-2
226	XPRP = 0.732 ACET + 0.268 ALDX + 0.268 PAR + XO2H + RO2	k = 1.00E+0	1.00E+0
227	XPAR = XO2N + RO2	Falloff: F=0.41; n=1 k(0) = 4.81E-20 k(inf) = 4.30E-1 (T/298)^-8	1.49E-1
228	XPAR = 0.126 ALDX + 0.874 ROR + 0.126 XO2H + 0.874 XO2 + RO2 - 0.126 PAR	k = 1.00E+0	1.00E+0
229	INTR = HNO3	k = 1.40E-4	1.40E-4
230	SO2 = SULF	k = 0.00E+0	0.00E+0
231	DMS + OH = SO2 + FORM + MEO2	k = 1.12E-11 exp(-250/T)	4.84E-12
232	DMS + OH + O2 = SULF + MEO2	k = 1.28E-37 exp(4480/T)	4.33E-31
233	DMS + NO3 = SO2 + FORM + MEO2 + HNO3	k = 1.90E-13 exp(520/T)	1.09E-12
234	NO2 + OH + H2O = HNO3 + H2O	k = 1.10E-30	1.10E-30

Notes:

(a) k_{298} is the rate constant at 298 K and 1 atmosphere using units in molecules/cm^3 and 1/s

(b) For photolysis reactions k_{298} shows the photolysis rate at a solar zenith angle of 60° and height of 600 m above ground and sea level

Table 3. The 152 reactions reviewed for CB6r5 along with reaction rate changes and data sources used.

No.	Reaction	k_{298} [a,b]	Ratio [c]	Comment [d]
1	NO2 = products	6.30E-03		IUPAC
2	O + O2 + M = products	6.11E-34	1.06	IUPAC
3	O3 + NO = products	1.89E-14	1.09	IUPAC
4	O + NO = products	2.26E-12	0.91 [e]	IUPAC
5	O + NO2 = products	9.91E-12	0.96	IUPAC
6	O + NO2 = products	2.09E-12	0.99	IUPAC; Corrected value of n in falloff expression
7	O + O3 = products	7.96E-15		IUPAC
8	O3 = products	3.33E-04		IUPAC
9	O3 = products	8.78E-06		IUPAC
10	O1D + M = products	3.28E-11		IUPAC
11	O1D + H2O = products	2.14E-10		IUPAC
12	O3 + OH = products	7.25E-14		IUPAC
13	O3 + HO2 = products	2.01E-15		IUPAC
14	OH + O = products	3.47E-11		IUPAC
15	HO2 + O = products	5.87E-11	1.03	JPL
16	OH + OH = products	1.48E-12		IUPAC
17	OH + OH = products	6.21E-12	1.18	IUPAC
18	OH + HO2 = products	1.11E-10		IUPAC
19	HO2 + HO2 = products	2.90E-12		IUPAC
20	HO2 + HO2 + H2O = products	6.53E-30		IUPAC
21	H2O2 = products	3.78E-06		IUPAC
22	H2O2 + OH = products	1.80E-12	1.06	IUPAC
23	H2O2 + O = products	1.70E-15		IUPAC
24	NO + NO + O2 = products	3.95E-38	2.02	IUPAC
25	HO2 + NO = products	8.54E-12		IUPAC
26	NO2 + O3 = products	3.52E-17		IUPAC
27	NO3 = products	1.56E-01		JPL
28	NO3 = products	1.98E-02		JPL
29	NO3 + NO = products	2.60E-11		IUPAC
30	NO3 + NO2 = products	6.56E-16		JPL
31	NO3 + O = products	1.70E-11		IUPAC
32	NO3 + OH = products	2.00E-11		IUPAC
33	NO3 + HO2 = products	4.00E-12		IUPAC
35	NO3 + NO3 = products	2.28E-16		JPL
36	NO3 + NO2 = products	1.24E-12		IUPAC
37	N2O5 = products	4.46E-02		IUPAC
38	N2O5 = products	2.52E-05		IUPAC
39	N2O5 + H2O = products	1.00E-22		IUPAC
40	NO + OH = products	9.77E-12		IUPAC
43	HONO = products	1.04E-03		IUPAC

No.	Reaction	k_{298} [a,b]	Ratio [c]	Comment [d]
44	HONO + OH = products	5.98E-12		IUPAC
45	NO2 + OH = products	1.06E-11		JPL
46	HNO3 + OH = products	1.54E-13		IUPAC
47	HNO3 = products	2.54E-07		IUPAC
48	HO2 + NO2 = products	7.50E-13	0.54	IUPAC
49	PNA = products	6.20E-02	0.75	IUPAC
50	PNA = products	2.36E-06		IUPAC
51	PNA + OH = products	3.24E-12		IUPAC
52	SO2 + OH = products	9.35E-13	1.15	IUPAC
53	C2O3 + NO = products	1.98E-11		IUPAC
54	C2O3 + NO2 = products	9.86E-12	1.05	IUPAC adjusted by +10% to reproduce the K_{eq} (k55/k54) at 298 K specified JPL in the discussion notes (2.3E-8) which is consistent with IUPAC (2.26E-8)
55	PAN = products	4.31E-04	1.44	IUPAC
56	PAN = products	3.47E-07		IUPAC
57	C2O3 + HO2 = products	2.20E-11	1.58	IUPAC; C2O3 + HO2
58	C2O3 + RO2 = products	1.60E-11	1.22	IUPAC; C2O3 + ethylperoxy
59	C2O3 + C2O3 = products	1.55E-11		IUPAC; C2O3 + C2O3
60	C2O3 + CXO3 = products	1.55E-11	1	Set equal to C2O3 + C2O3; (new implementation, no change to rate constant)
61	CXO3 + NO = products	2.10E-11		IUPAC; peroxypropionyl + NO
62	CXO3 + NO2 = products	8.28E-12	0.88	Set to k54 (PAN formation) and adjusted as k63 so that K_{eq} (k63/k62) is the same as for PAN from IUPAC
63	PANX = products	3.62E-04	1.21	Set to k55 (PAN dissociation) adjusted by the ratio of PPN to PAN dissociation rates (3.6/4.3) at 298 K and 1 atm from IUPAC
64	PANX = products	3.47E-07		IUPAC
65	CXO3 + HO2 = products	2.20E-11	1.58	Set equal to C2O3 + HO2
66	CXO3 + RO2 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
67	CXO3 + CXO3 = products	1.55E-11	0.91	Set equal to C2O3 + C2O3
68	RO2 + NO = products	8.03E-12		CB6 representative RO2 + NO rate
69	RO2 + HO2 = products	7.03E-12		CB6 representative RO2 + HO2 rate
70	RO2 + RO2 = products	3.48E-13		CB6 representative RO2 + RO2 rate
71	MEO2 + NO = products	7.70E-12		IUPAC
72	MEO2 + HO2 = products	5.21E-12		IUPAC
73	MEO2 + C2O3 = products	1.07E-11		IUPAC
74	MEO2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
75	XO2H + NO = products	9.04E-12		IUPAC; considering primarily ethylperoxy and hydroxyethylperoxy radicals
76	XO2H + HO2 = products	9.96E-12		IUPAC; considering ethylperoxy and hydroxyethylperoxy radicals
77	XO2H + C2O3 = products	1.60E-11	1.22	IUPAC; set equal to C2O3 + RO2

No.	Reaction	k_{298} [a,b]	Ratio [c]	Comment [d]
78	XO2H + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
79	XO2 + NO = products	9.04E-12		Set equal to CB6 representative RO2 + NO rate
80	XO2 + HO2 = products	9.96E-12		Set equal to CB6 representative RO2 + HO2 rate
81	XO2 + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
82	XO2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
83	XO2N + NO = products	9.04E-12		Set equal to CB6 representative RO2 + NO rate
84	XO2N + HO2 = products	9.96E-12		Set equal to CB6 representative RO2 + HO2 rate
85	XO2N + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
86	XO2N + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
87	MEPX + OH = products	1.00E-11		IUPAC
89	ROOH + OH = products	1.00E-11		IUPAC
90	ROOH = products	2.68E-06		Set equal to MEPX photolysis
93	FACD + OH = products	4.50E-13		IUPAC
94	AACD + OH = products	6.93E-13		IUPAC
96	FORM + OH = products	8.49E-12		IUPAC
97	FORM = products	1.69E-05	0.95	IUPAC
98	FORM = products	2.69E-05	1.13	IUPAC
99	FORM + NO3 = products	5.50E-16		IUPAC
104	ALD2 + OH = products	1.50E-11		IUPAC
105	ALD2 + NO3 = products	2.73E-15		IUPAC
106	ALD2 = products	1.96E-06	1.11	IUPAC
107	ALDX + OH = products	1.91E-11		IUPAC
108	ALDX + NO3 = products	6.30E-15		IUPAC
109	ALDX = products	2.62E-05	3.77	IUPAC data sheet P24 for i-C3H7CHO
110	GLYD + OH = products	8.00E-12		IUPAC
111	GLYD = products	2.76E-06	1.76	IUPAC
112	GLYD + NO3 = products	2.73E-15	1	Set equal to NO3 + ALD2 (new implementation, no change to rate constant)
113	GLY + OH = products	9.70E-12		IUPAC
114	GLY = products	5.01E-04	9.11	IUPAC
115	GLY + NO3 = products	4.00E-16	0.15	IUPAC
117	MGLY + NO3 = products	5.00E-16	0.18	IUPAC
118	MGLY + OH = products	1.31E-11		IUPAC
119	H2 + OH = products	6.70E-15		IUPAC
120	CO + OH = products	2.28E-13		IUPAC
121	CH4 + OH = products	6.37E-15		IUPAC
122	ETHA + OH = products	2.41E-13		IUPAC
123	MEOH + OH = products	8.95E-13		IUPAC

No.	Reaction	k_{298} [a,b]	Ratio [c]	Comment [d]
124	ETOH + OH = products	3.21E-12		IUPAC
127	ACET + OH = products	1.76E-13		IUPAC
128	PRPA + OH = products	1.07E-12		IUPAC
133	ETHY + OH = products	7.52E-13		IUPAC
134	ETH + OH = products	7.84E-12		IUPAC
135	ETH + O3 = products	1.55E-18	0.98	IUPAC
136	ETH + NO3 = products	2.10E-16		IUPAC
139	OLE + NO3 = products	9.54E-15		IUPAC
142	IOLE + NO3 = products	3.70E-13		IUPAC
146	ISO2 + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
147	ISO2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
161	EPX2 + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
162	EPX2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
169	BZO2 + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
171	BZO2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
174	TO2 + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
176	TO2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
180	XLO2 + C2O3 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
181	XLO2 + RO2 = products	3.48E-13		Set equal to CB6 representative RO2 + RO2 rate
199	OPO3 + NO = products	2.10E-11	2.10	Set equal to CXO3 + NO
200	OPO3 + NO2 = products	8.28E-12	0.88	Set equal to PANX formation
201	OPAN = products	3.62E-04	1.21	Set equal to PANX dissociation
202	OPO3 + HO2 = products	2.20E-11	1.58	Set equal to C2O3 + HO2
203	OPO3 + C2O3 = products	1.55E-11		Set equal to C2O3 + C2O3
204	OPO3 + RO2 = products	1.60E-11	1.22	Set equal to C2O3 + RO2
208	ECH4 + OH = products	6.37E-15		IUPAC
209	I2 = products	1.44E-01		IUPAC
210	HOI = products	6.36E-02		IUPAC
211	I + O3 = products	1.30E-12		IUPAC
212	IO = products	1.18E-01		IUPAC
213	IO + IO = products	9.88E-11		IUPAC
214	IO + HO2 = products	8.57E-11		IUPAC
215	IO + NO = products	1.96E-11		IUPAC
216	IO + NO2 = products	3.54E-12	0.997	IUPAC; Corrected value of n in falloff expression
217	OIO = products	1.41E-01		JPL
218	OIO + OH = products	3.96E-10	0.84	Revised value of n in falloff expression; Plane et al. (2006) https://doi.org/10.1021/jp055364y
220	OIO + NO = products	6.78E-12		IUPAC
231	DMS + OH = products	4.84E-12		IUPAC

No.	Reaction	k_{298} [a,b]	Ratio [c]	Comment [d]
232	DMS + OH + O2 = products	4.33E-31		IUPAC; Derived a simpler rate expression than recommended by IUPAC
233	DMS + NO3 = products	1.09E-12		IUPAC
234	NO2 + OH + H2O = products	1.10E-30		Derived from doi.org/10.5194/acp-20-3091-2020 as a 3rd order reaction that can be implemented in any model

Notes:
(a) k_{298} is the rate constant at 298 K and 1 atmosphere using units in molecules/cm^3 and 1/s
(b) For photolysis reactions k_{298} shows the photolysis rate at a solar zenith angle of 60° and height of 600 m above ground and sea level
(c) Ratio of k_{298} for CB6r5 to CB6r4 at 1 atm; blank where the rate constant was reviewed and no change made; 1 where the rate constant implementation changed without changing the rate constant
(d) IUPAC data from http://iupac.pole-ether.fr; JPL data from https://jpldataeval.jpl.nasa.gov/
(e) Ratio accounts for change in reaction form from 3rd order (with reactant M) to 2nd order with a rate constant that depends on M (i.e., a Troe expression)

6.0 MECHANISM TESTING

We tested CB6r5 mechanism updates in CAMx simulations of June, 2012 using model inputs provided by the TCEQ. To conduct several sensitivity simulations efficiently we focused on a multi-day high ozone period of June 5-8, 2012, that saw high ozone in most urban areas of eastern Texas. We reviewed maps of model species concentrations, e.g., for ozone (O_3). We averaged concentrations over the time period from 11 am to 3 pm when photochemical activity tends to peak due to strong sunlight and warm temperatures.

We also used the chemical process analysis (CPA) probing tool in CAMx to output information on how chemical reactions influenced model species concentrations during simulations (Ramboll, 2018). We implemented CPA for CB6r5. We prepared maps of CPA parameters averaged over the same hours and dates as for CAMx species concentrations, namely 11 am to 3 pm of June 5-8, 2012.

We conducted nine CAMx sensitivity simulations to understand the importance of CB6r5 updates for groups of chemical reactions and the results are discussed below. Table 4 lists which rate constant updates (from CB6r5d1) are applied in each sensitivity test. For example, the test named "Photolysis reaction rates" applies CB6r5d1 updates to photolysis reactions only, leaving all other reaction rates the same as CB6r4. The test named "Stoichiometry changes" keeps all rate constants at their CB6r4 values but applies the CB6r5 updates to product yields so that their impact can be quantified. The test named "OH + NO2 + H2O reaction" adds one new reaction to the CB6r5d1 updates so that its impact can be quantified.

Table 4. CAMx sensitivity simulations performed to understand the importance of CB6r5 updates for groups of chemical reactions

No.	Reaction	CB6r5d1	Photolysis reaction rates	PAN reaction rates	OH + NO2 reaction rate	O3 + NO reaction rate	NO + NO reaction rate	Iodine reaction rates	RO2 reaction rates	Stoichiometry changes [a]	OH + NO2 + H2O reaction [b]
2	O + O2 + M = products	Y									Y
3	O3 + NO = products	Y				Y					Y
4	O + NO = products	Y									Y
5	O + NO2 = products	Y									Y
6	O + NO2 = products	Y									Y
15	HO2 + O = products	Y									Y
17	OH + OH = products	Y									Y
22	H2O2 + OH = products	Y									Y
24	NO + NO + O2 = products	Y					Y				Y
45	NO2 + OH = products	Y			Y						Y
48	HO2 + NO2 = products	Y		Y							Y
49	PNA = products	Y		Y							Y
52	SO2 + OH = products	Y									Y
54	C2O3 + NO2 = products	Y		Y							Y
55	PAN = products	Y		Y							Y
57	C2O3 + HO2 = products	Y							Y		Y
58	C2O3 + RO2 = products	Y							Y		Y
62	CXO3 + NO2 = products	Y		Y							Y
63	PANX = products	Y		Y							Y
65	CXO3 + HO2 = products	Y							Y		Y
66	CXO3 + RO2 = products	Y							Y		Y
67	CXO3 + CXO3 = products	Y							Y		Y
77	XO2H + C2O3 = products	Y							Y		Y
81	XO2 + C2O3 = products	Y							Y		Y
85	XO2N + C2O3 = products	Y							Y		Y
97	FORM = products	Y	Y								Y
98	FORM = products	Y	Y								Y
106	ALD2 = products	Y	Y								Y
109	ALDX = products	Y	Y								Y
111	GLYD = products	Y	Y								Y
114	GLY = products	Y	Y								Y
115	GLY + NO3 = products	Y									Y
117	MGLY + NO3 = products	Y									Y

No.	Reaction	CB6r5d1	Photolysis reaction rates	PAN reaction rates	OH + NO2 reaction rate	O3 + NO reaction rate	NO + NO reaction rate	Iodine reaction rates	RO2 reaction rates	Stoichiometry changes [a]	OH + NO2 + H2O reaction [b]
135	ETH + O3 = products	Y									Y
146	ISO2 + C2O3 = products	Y							Y		Y
161	EPX2 + C2O3 = products	Y							Y		Y
169	BZO2 + C2O3 = products	Y							Y		Y
174	TO2 + C2O3 = products	Y							Y		Y
180	XLO2 + C2O3 = products	Y							Y		Y
199	OPO3 + NO = products	Y		Y							Y
200	OPO3 + NO2 = products	Y		Y							Y
201	OPAN = products	Y		Y							Y
202	OPO3 + HO2 = products	Y							Y		Y
204	OPO3 + RO2 = products	Y							Y		Y
216	IO + NO2 = products	Y						Y			Y
218	OIO + OH = products	Y						Y			Y
234	OH + NO2 +H2O = products										Y

Notes:
(a) The sensitivity test "stoichiometry changes" did not update any rate constant but did update product stoichiometric coefficients for CB6r5
(b) The sensitivity test "OH + NO2 + H2O reaction" is not the same as CB6r5d3 because it lacks the final updates to OH + NO2 and PAN/PANX/OPAN rate constants of CB6r5d3

We used CAMx version 7 with model inputs developed by the TCEQ for June 2012 and model options shown in Table 5.

Table 5. CAMx model options

Science Options	CAMx Base Case setup
Version	Version 7.0
Vertical Grid Mesh	29 Layers (TCEQ's CAMx vertical structure)
Time Zone	CST
Chemistry mechanism	CB6r4 or CB6r5 gas-phase mechanism
Horizontal Grids	4 km nested within 12 km and 36 km
Meteorology	TCEQ's 2012 WRF meteorology
Photolysis mechanism	TUV version 4.8 with TOMS ozone column data
Advection Scheme	Piecewise Parabolic Method (PPM)
Cloud convection scheme	On / Relaxed Arakawa-Schubert
Planetary Boundary Layer (PBL) mixing	K-theory/ KV100 patch
In-line IX emissions	Oceanic iodine (Ix) emissions computed from saltwater masks

Science Options	CAMx Base Case setup
Chemistry Solver	EBI
Parallelization	MPI and OMP

6.1 Model Species Concentrations: Texas 4 km Grid

CB6r5 tends to increase ozone (O_3) over Texas during the high ozone period as shown in Figure 1. O_3 increases with CB6r5d1 are generally less than 0.3 ppb over the Gulf but greater than 1 ppb over land, and wide areas exceeding 3 ppb increase over in eastern Texas. CB6r5d3 moderates the O_3 increases over land, with the only a small area seeing 3 ppb increase and reverses the sign O_3 changes over the Gulf to O_3 decreases of up to about 1 ppb.

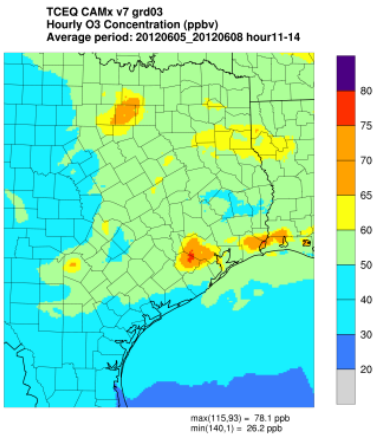
CB6r5 tends to increase nitrogen dioxide (NO_2) over Texas with exceptions being the Dallas/Fort Worth (DFW) area and Galveston Bay (Figure 2). NO_2 increases with CB6r5d1 are small, generally tenths of a ppb, but in areas where O_3 production is NOx-limited a small NO_2 increase in can enhance O_3 production. CB6r5d3 moderates the NO_2 increases over land and mostly reverses the sign NO_2 changes over the Gulf to decreases. The changes from CB6r5d1 to CB6r5d3 influence NO_2 availability in more rural areas over land (PAN and OH + NO_2 rate constant changes) and especially over the Gulf of Mexico (added OH + NO_2 + H_2O reaction).

Changes in PAN, nitric acid (HNO_3), and formaldehyde due to CB6r5 updates are shown in Figure 3 for the Texas 4 km grid. PAN rate constant changes reduce PAN over land by about a tenth of a ppb, consistent with widespread NO_2 increases seen in Figure 2. HNO_3 increases with CB6r5 consistent with less nitrogen being sequestered in PAN and a new HNO_3 forming reaction being added in CB6r5 (OH + NO_2 + H_2O = HNO_3 + H_2O). Formaldehyde (CB6 species FORM) increases with CB6r5 over land (except near urban areas such as DFW and Houston) but decreases over the Gulf. However, the changes in formaldehyde are small at around a tenth of a ppb.

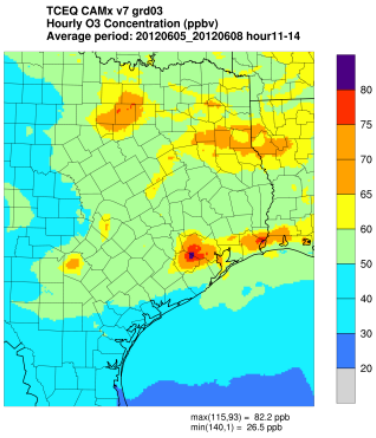
Radicals (e.g., hydroxyl radical OH) are highly reactive species and essential to photochemistry in the atmosphere. Changes to OH, HO_2 and RO_2 radical concentrations due to CB6r5 are shown in Figure 4. CB6r5 increases OH radical over land but decreases OH over the Gulf. O_3 photolysis is a major source of OH which can explain the similar spatial patterns seen for and O_3 and OH changes. Decreases in OH over the Gulf also are consistent with adding a new reaction that removes OH (OH + NO_2 + H_2O = HNO_3 + H_2O) which is most important in humid regions such as the Gulf. HO_2 changes have similar spatial patterns to OH because HO_2 is produced by many reactions of OH with VOCs. Spatial patterns in RO_2 changes with CB6r5 are more complex than for OH and HO_2. RO_2 with is produced by many reactions of OH with VOCs and is removed by reactions HO_2 and NO, thus RO_2 concentration changes are influenced by changes in several species as well as changes to rate constants for several RO_2 reactions.

Adding the reaction OH + NO_2 + H_2O = HNO_3 + H_2O in CB6r5d3 caused several concentration changes that are consistent and, to some extent, synergistic. This reaction consumes OH and lowers the OH concentration, more so where humidity is high. The reaction also consumes NO_2 and consequently tends to lower O_3 concentration. Lower O_3 reduces the amount of OH produced by O_3 photolysis and thus lowers OH concentration, which acts synergistically with direct OH removal by the added reaction.

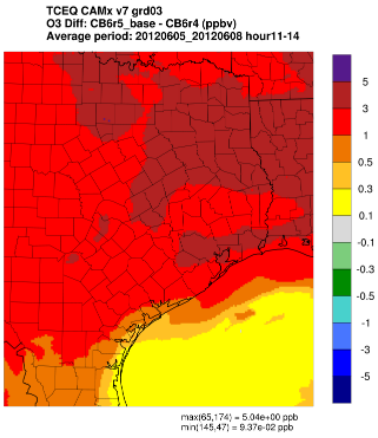
CB6r4



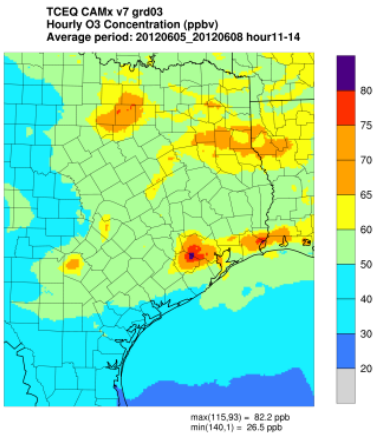
CB6r5d1



CB6r5d1 – CB6r4



CB6r5d3



CB6r5d3 – CB6r4

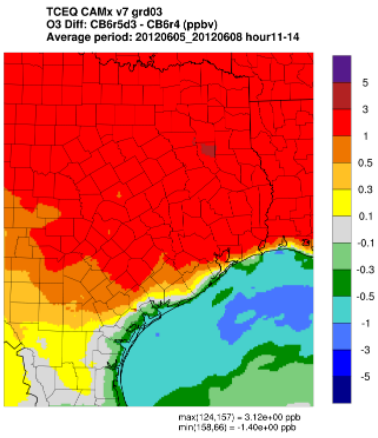
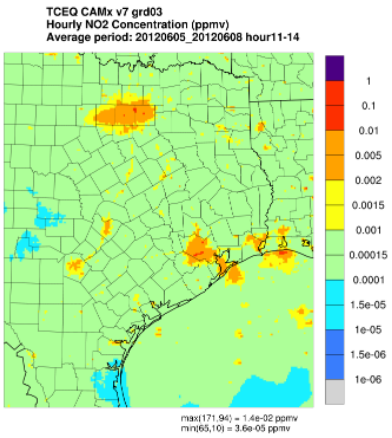
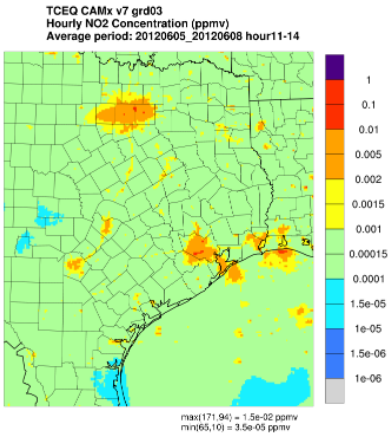


Figure 1. **O_3 (ppb) over the Texas 4 km grid with CB6r4, CB6r5d1 and CB6r5d3 averaged over hours 11 am to 3 pm on June 5-8, 2012 and concentration differences for CB6r5d1 – CB6r4 and CB6r5d3 – CB6r4.**

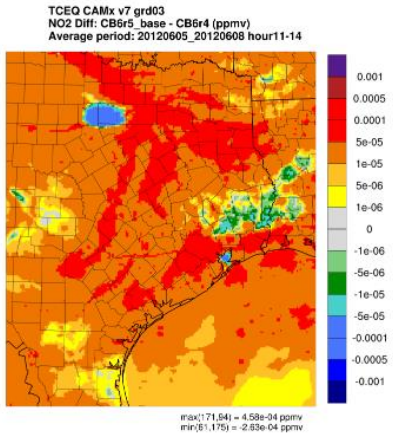
CB6r4



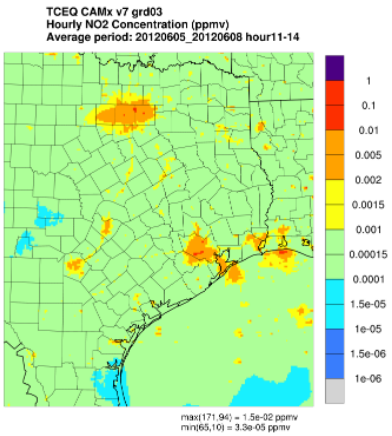
CB6r5d1



CB6r5d1 – CB6r4



CB6r5d3



CB6r5d3 – CB6r4

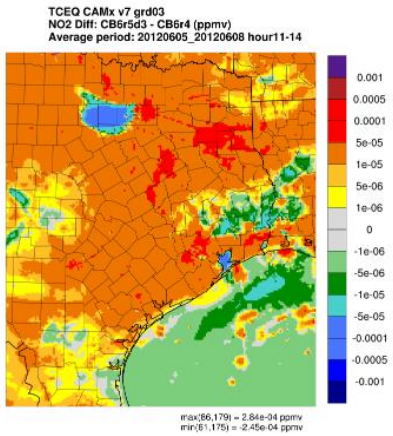


Figure 2. **NO_2 (ppb) over the Texas 4 km grid with CB6r4, CB6r5d1 and CB6r5d3 averaged over hours 11 am to 3 pm on June 5-8, 2012 and concentration differences for CB6r5d1 – CB6r4 and CB6r5d3 – CB6r4.**

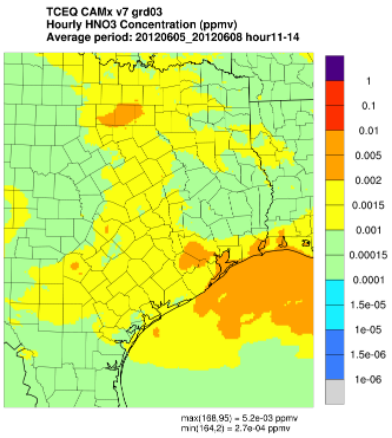
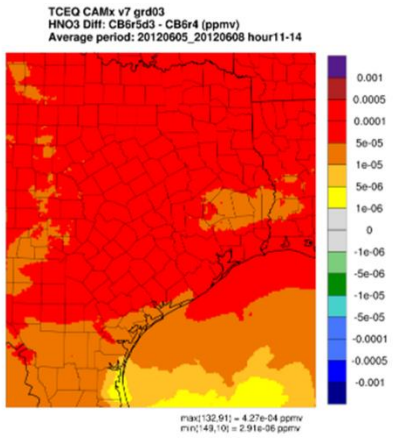
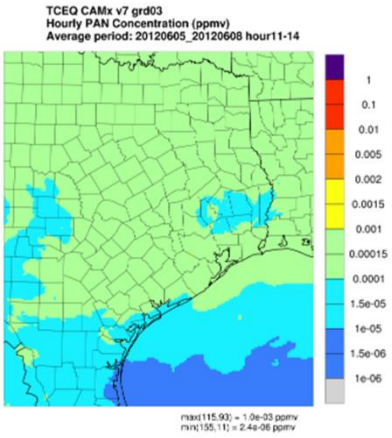
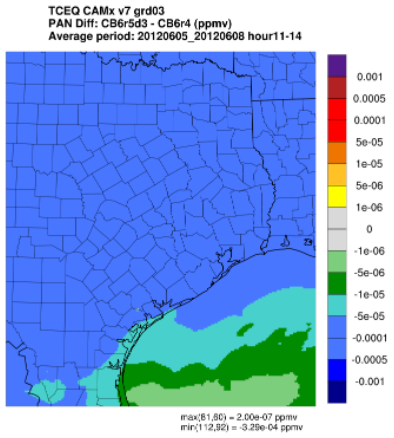
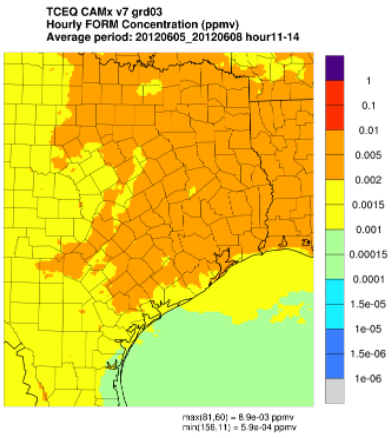
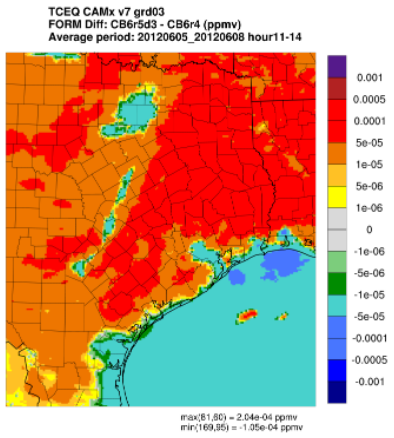
HNO3 CB6r5d3	ΔHNO3 CB6r5d3 – CB6r4
	
PAN CB6r5d3	ΔPAN CB6r5d3 – CB6r4
	
FORM CB6r5d3	ΔFORM CB6r5d3 – CB6r4
	

Figure 3. **HNO_3, PAN and formaldehyde (ppb) over the Texas 4 km grid with CB6r5d3, and differences from CB6r4, averaged over hours 11 am to 3 pm on June 5-8, 2012.**

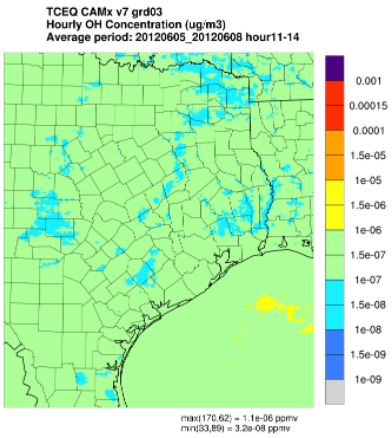
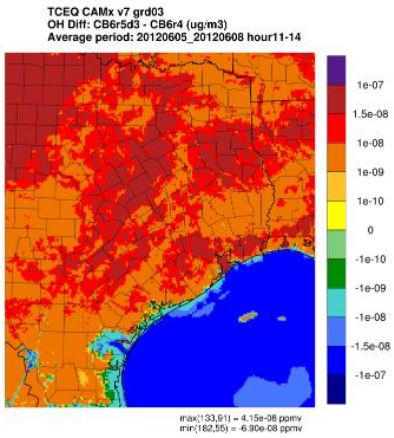
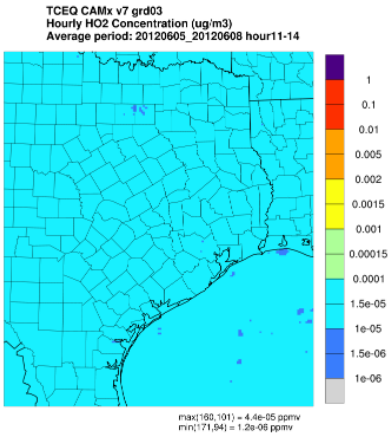
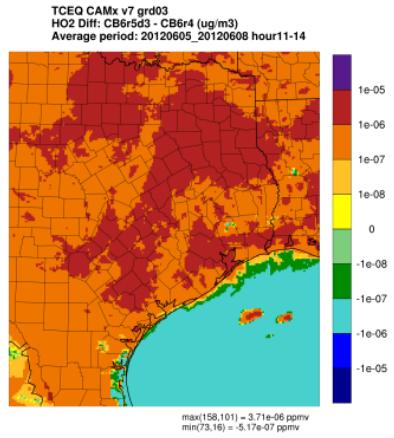
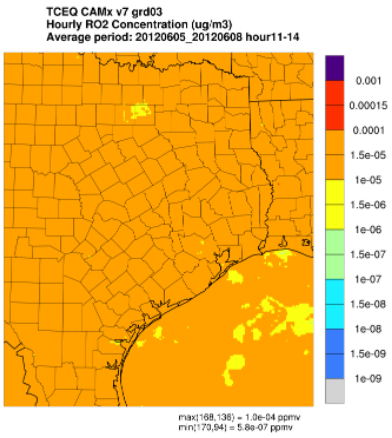
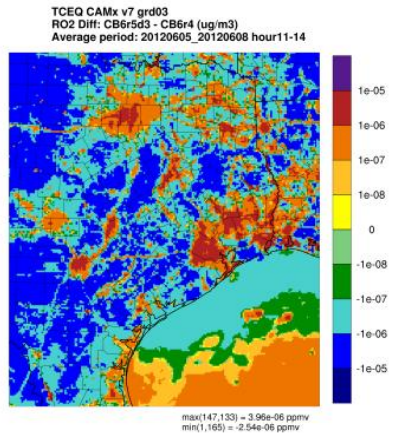
OH CB6r5d3	ΔOH CB6r5d3 – CB6r4
	
HO2 CB6r5d3	ΔHO2 CB6r5d3 – CB6r4
	
RO2 CB6r5d3	ΔRO2 CB6r5d3 – CB6r4
	

Figure 4. **OH, HO_2 and RO_2 radicals (ppb) over the Texas 4 km grid with CB6r5d3, and differences from CB6r4, averaged over hours 11 am to 3 pm on June 5-8, 2012.**

6.2 CPA Results: Texas 4 km Grid

We plotted CAMx CPA output averaged over the same time period as for species concentrations to help understand how CB6r5 mechanism updates influence changes in species concentrations. CPA information is fundamentally different from CAMx concentrations in that CPA parameters are not transported between grid cells by advection and diffusion. Thus, maps CPA parameters, e.g. O_3 production rate, can reveal differences between neighboring grid cells that are difficult to see from concentration maps because of transport between grid cells.

CPA information for O_3 production and destruction rates is shown in Figure 5. Stronger O_3 production is strongly associated with emissions from urban and industrialized areas such as DFW, Houston, the I-35 corridor and power generation in Northeast Texas. The CB6r5 updates tend to reduce O_3 production in urban areas but increase O_3 production in more rural areas. The CPA parameter "O_3 production in VOC-limited areas" counts only O_3 production that is classified as VOC-limited at the time of the O_3 production. Grid cells are classified as VOC-limited when the ratio of production rates of HNO_3 to H_2O_2 is above 0.35 (Ramboll, 2018). For the times/dates shown, most of the regions classified as VOC-limited see decreased O_3 production rates after the CB6r5 updates.

Photochemical reactions can destroy O_3 simultaneous with O_3 production. The CPA parameter "O_3 destruction" shows that the CB6r5 updates lead to more O_3 destruction over the Gulf but less O_3 destruction over land. Reduced O_3 destruction contributes to generally higher O_3 concentrations over land with CB6r5 compared to CB6r4.

CPA information for OH radical production and removal via OH + NO_2 reaction is shown in Figure 6. "New OH" is the total production rate (ppb/hr) of OH radicals whereas "OH from O_3 photolysis" is only the OH production that results from O_3 photolysis. O_3 photolysis reactions in CB6r5 and CB6r4 are the same, but more O_3 with CB6r5 causes more OH production from O_3 photolysis. The CPA results confirm that O_3 photolysis is a dominant contributor to OH production, and increased O_3 with CB6r5 largely explains the increased OH production with CB6r5. One consequence of increased OH production with CB6r5 is greater HNO_3 production via OH + NO_2 reaction.

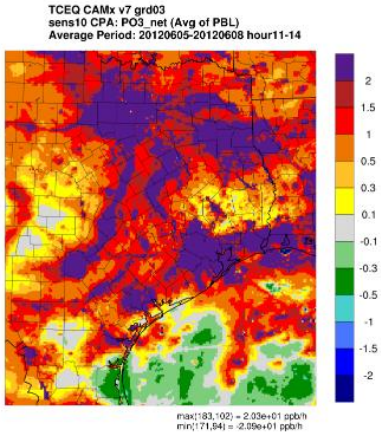
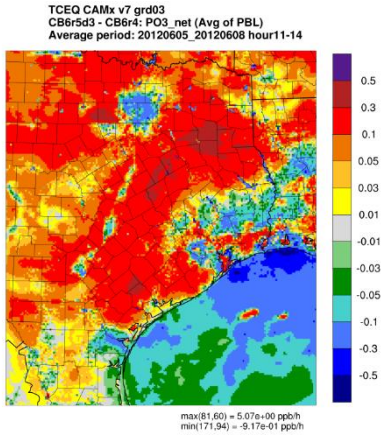
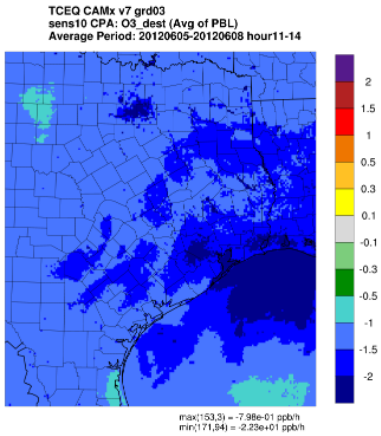
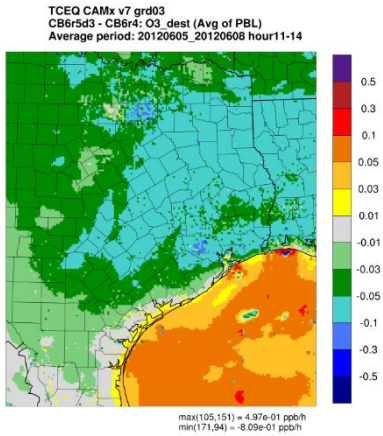
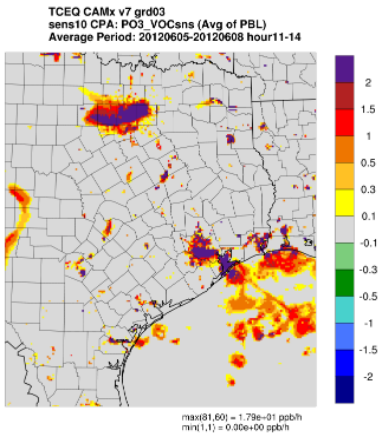
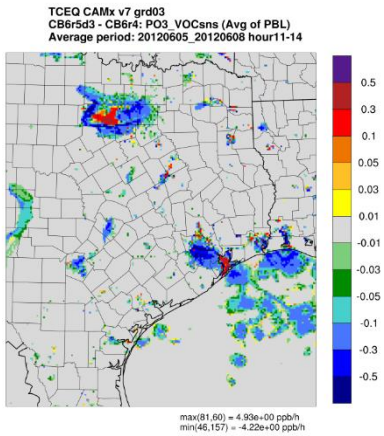
O_3 Production CB6r5d3	Δ O_3 Production CB6r5d3 – CB6r4
	
O_3 Destruction CB6r5d3	Δ O_3 Destruction CB6r5d3 – CB6r4
	
VOC-limited O_3 Production CB6r5d3	Δ VOC-limited O_3 Prod. CB6r5d3 – CB6r4
	

Figure 5. **CPA diagnostic information (ppb/hr) for O_3 production and destruction over the Texas 4 km grid with CB6r5d3, and differences from CB6r4, averaged over hours 11 am to 3 pm on June 5-8, 2012.**

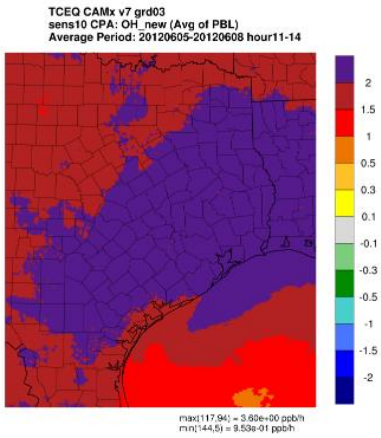
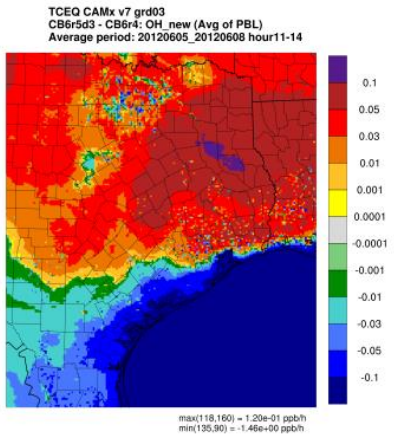
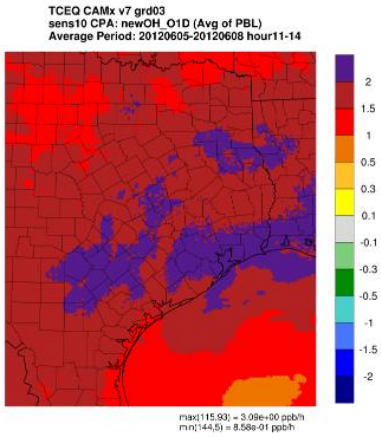
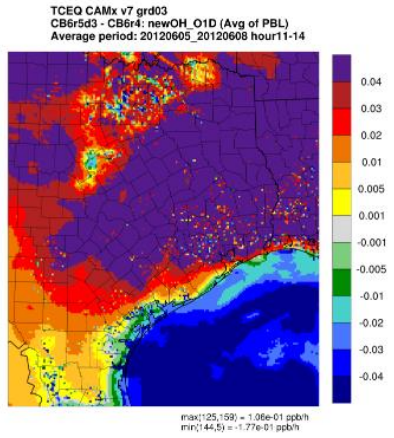
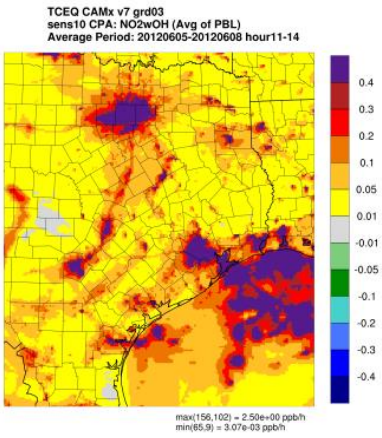
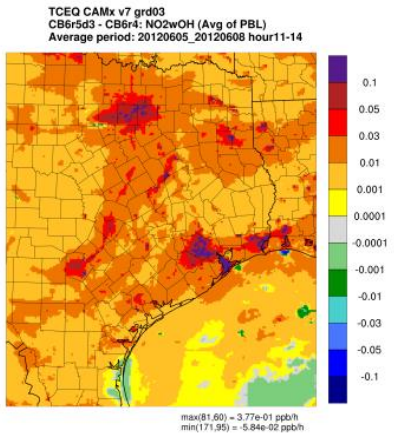
New OH CB6r5d3	Δ new OH CB6r5d3 – CB6r4
	
New OH from O3 photolysis CB6r5d3	Δ OH from O3 photolysis CB6r5d3 – CB6r4
	
OH + NO_2 CB6r5d3	Δ (OH + NO_2) CB6r5d3 – CB6r4
	

Figure 6. **CPA diagnostic information (ppb/hr) for OH radical production and removal via OH + NO_2 reaction over the Texas 4 km grid with CB6r5d3, and differences from CB6r4, averaged over hours 11 am to 3 pm on June 5-8, 2012.**

6.3 Results for CONUS 36 km Grid

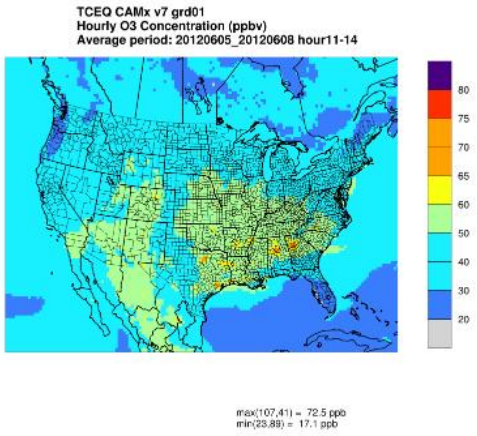
We examined CAMx results for the Continental US (CONUS) 36 km grid to understand how they compared to 4 km grid results. We average results for the same time period with high O_3 across eastern Texas, although this may not be a high O_3 period for all parts of the CONUS. CB6r5 increases O_3 throughout the CONUS with parts of the Southeast and Northeast seeing O_3 increases comparable to Texas (Figure 7). CB6r5d3 moderates O_3 increases compared to CB6r5d1 throughout the CONUS. Near-coast waters of the Gulf of Mexico see the largest O_3 decreases with CB6r5d3 (compared to CB6r4) although parts of the Atlantic and Pacific also see O_3 decreases.

Results from the CAMx sensitivity tests (defined in Table 4) show which CB6r5 mechanism updates cause O_3 increases and decreases (Figure 8):

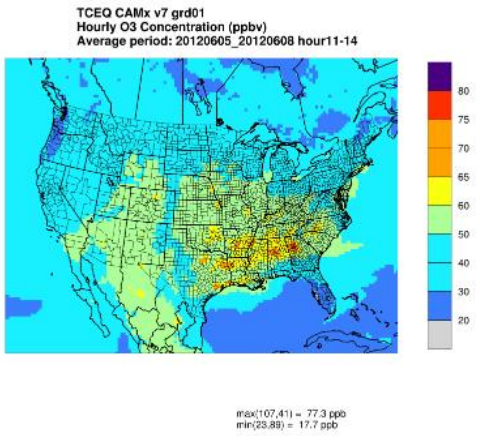
- The following update groups tend to increase O_3: photolysis reactions; PAN reactions: RO_2 reactions; Stoichiometry changes
- The following updates (single reaction changes) tend to decrease O_3: O_3 + NO reaction; OH + NO_2 + H_2O reaction
- The following updates have little impact on O_3: NO + NO reaction; Iodine reactions
- Figure 7 shows that the OH + NO_2 update of CB6r5d1 increased O_3 but this update was reverted (set back to CBr4) in CB6r5d3.

Similarly, the CAMx sensitivity tests reveal which CB6r5 mechanism updates increase and decrease OH radical (Figure 9) and the findings are the same as for O_3 changes.

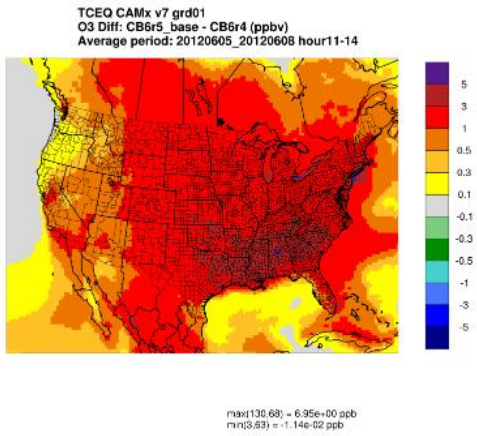
CB6r4



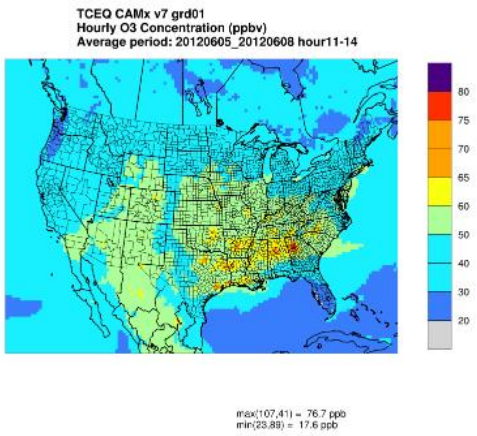
CB6r5d1



CB6r5d1 – CB6r4



CB6r5d3



CB6r5d3 – CB6r4

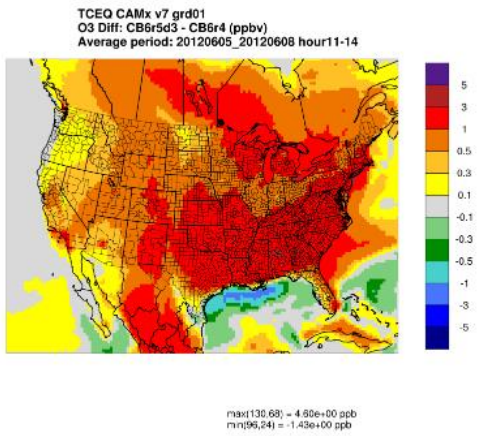


Figure 7. **O_3 (ppb) over the CONUS 36 km grid with CB6r4, CB6r5d1 and CB6r5d3 averaged over hours 11 am to 3 pm on June 5-8, 2012 and concentration differences for CB6r5d1 – CB6r4 and CB6r5d3 – CB6r4.**

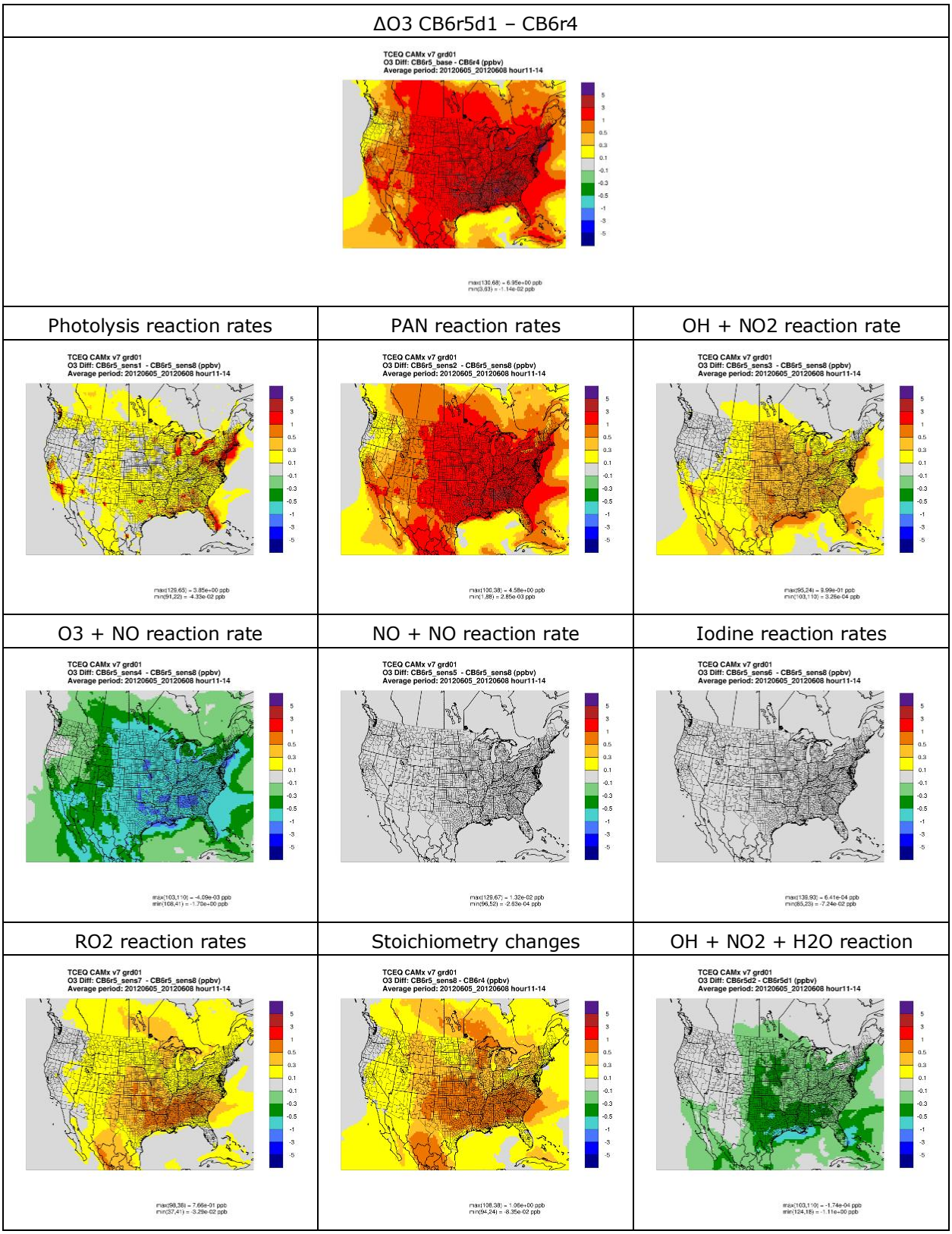


Figure 8. Contributions of CB6r5d1 updates and the OH + NO2 + H2O reaction added in CB6r5d3 to O_3 changes (ppb) over the CONUS 36 km grid (CB6r5d1 – CB6r4) averaged over hours 11 am to 3 pm on June 5-8, 2012.

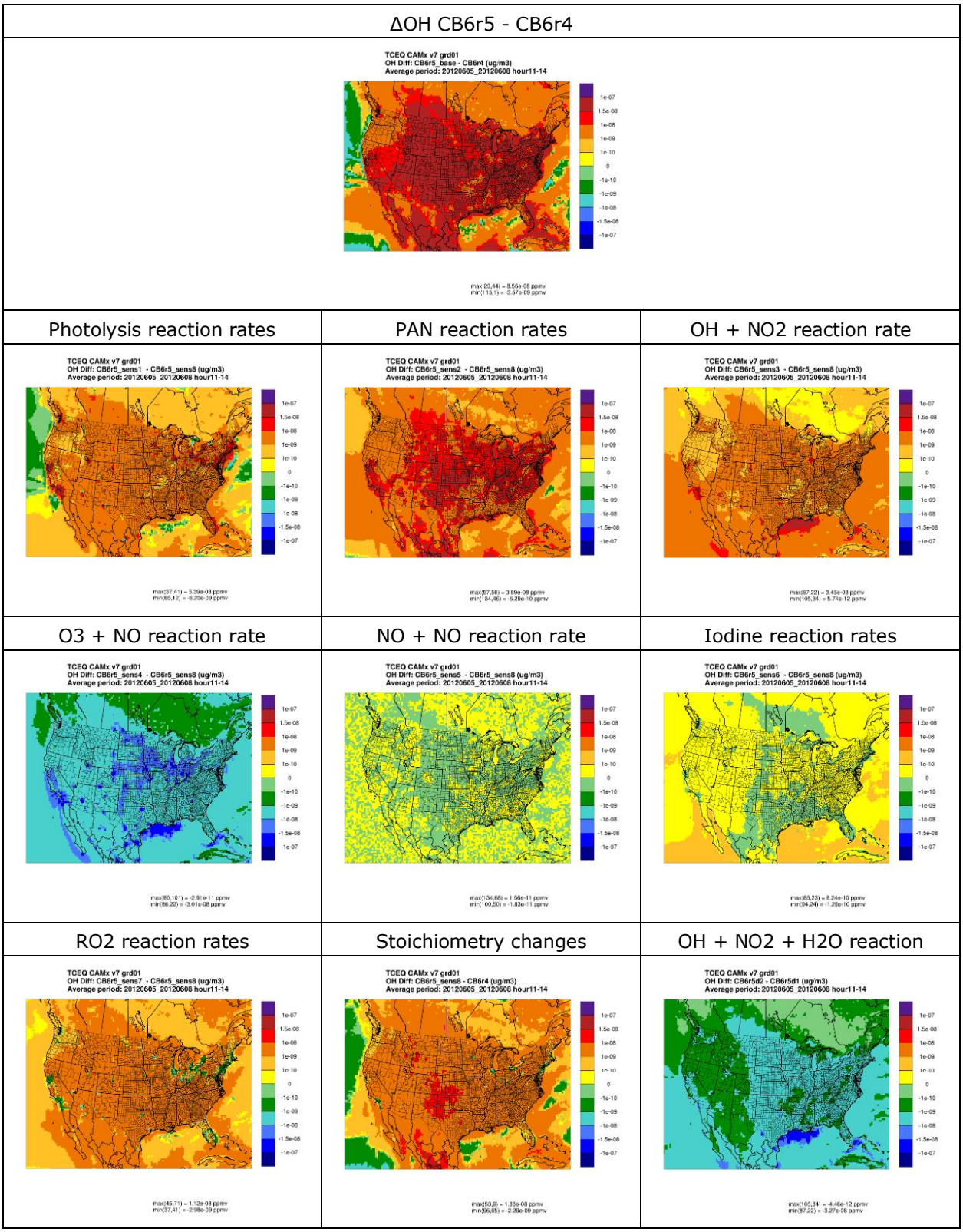


Figure 9. Contributions of CB6r5d1 updates and the OH + NO2 + H2O reaction added in CB6r5d3 to changes in O_3 production (ppb) over the CONUS 36 km grid (CB6r5d1 – CB6r4) averaged over hours 11 am to 3 pm on June 5-8, 2012.

6.4 Ozone Model Performance Evaluation

We quantified impacts of mechanism updates to O_3 model performance by comparing modeled 8-hour average O_3 from 11 AM to 7 PM CST for each day in June 2012 to observations at 109 Continuous Ambient Monitoring Stations (CAMS) within the 4 km East Texas model domain. We computed statistical metrics following recommendations of Emery et al. (2017) and results for CB6r4 and CB6r5 (i.e., CB6r5d3) are shown in Table 6. Statistical metrics for individual CAMS are provided for CB6r4 and CB6r5d3 in Table S-1 and Table S-2 of the Supplemental Information, respectively.

Model performance for O_3 was similar for both mechanisms, but the tendency of CB6r5 to predict higher O_3 than CB6r4 produced slightly more positive bias (5.8 ppb compared to 5.4 ppb) and larger error (8.1 ppb compared to 8.0 ppb) with CB6r5 than CB6r4. Emery et al. (2017) provide model performance benchmarks for normalized mean bias (NMB), normalized mean error (NME), and the correlation coefficient (r) that include "goals" representing the best a model can be expected to achieve and "criteria" that represent what most past modeling applications have achieved. Both mechanisms meet the criteria for NMB (<±15%) and NME (<25%) and the goal for r (>0.75) as seen in Table 6. Time-series of 8-hour ozone at five monitoring sites across eastern Texas also show that model results with CB6r4 and CB6r5 are very similar (Figure 10).We conclude that evaluating model performance for O_3 is unable to assess the validity of CB6r5 mechanism updates considering that the impacts of other model uncertainties (e.g., emissions, deposition and BCs) are considerably larger (Dunker et al., 2020) than the differences due to mechanism updates.

Table 6. Model performance statistics for average daily 8-hour ozone from 11 AM to 7 PM in June, 2012 for the CB6r4 and CB6r5 mechanisms

Statistical Metric	CB6r4	CB6r5
Number of Observations	3012	3012
Average Concentration - Observations (ppb)	46.1	46.1
Average Concentration - Model (ppb)	51.5	51.9
r^2	0.83	0.83
Mean Bias (ppb)	5.4	5.8
Mean Error (ppb)	8.0	8.1
Normalized Mean Bias (%)	11.8	12.6
Normalized Mean Error (%)	17.3	17.5
Mean Fractional Bias (%)	15.2	15.8
Mean Fractional Error (%)	19.3	19.3

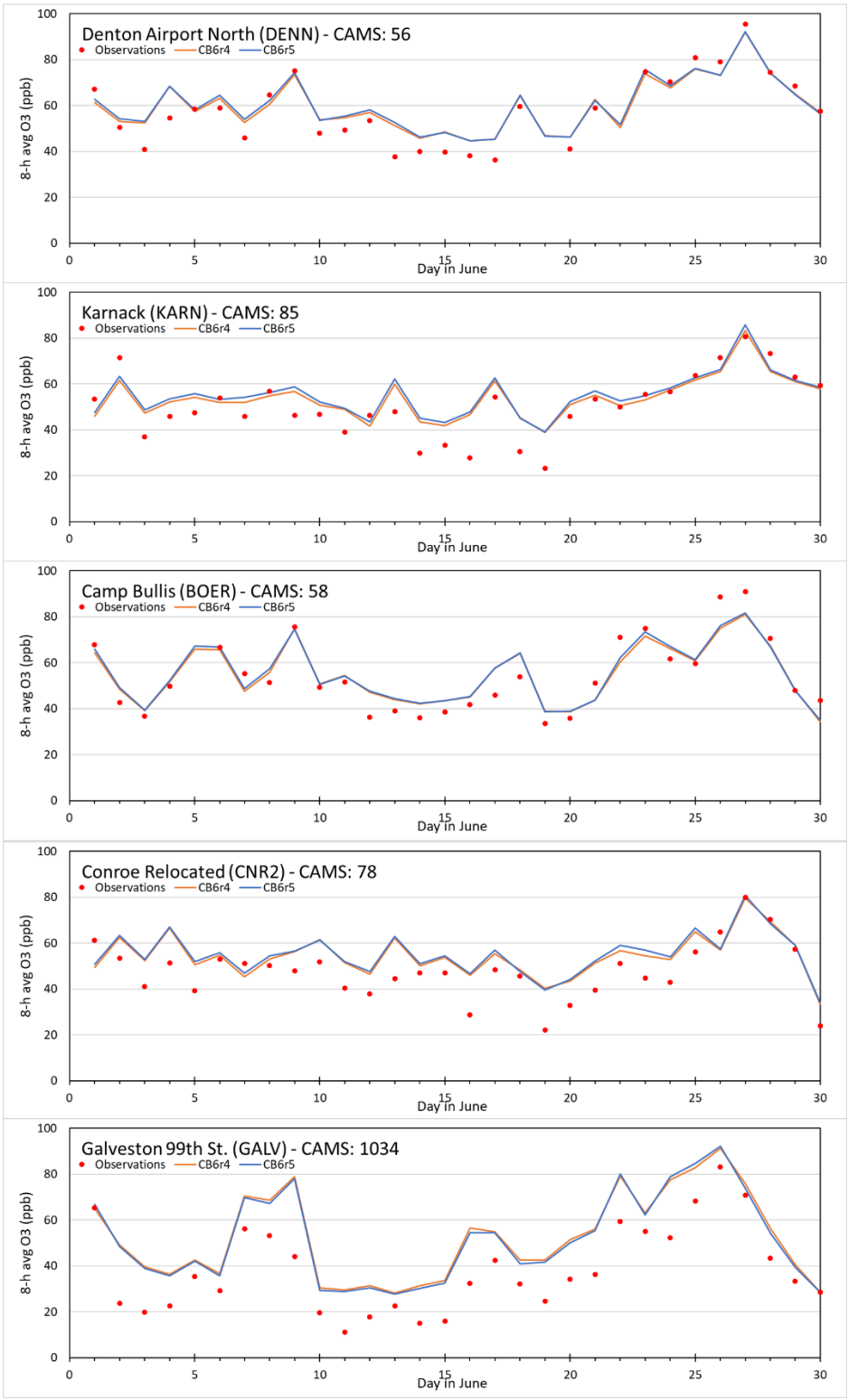


Figure 10. Time-series of daily 8-hour ozone from 11 AM to 7 PM in June 2012 with CB6r4, CB6r5 and observed at CAMS near Denton (CAMS 56), Karnack (CAMS 85), Camp Bullis (CAMS 58), Conroe (CAMS 78) and Galveston (CAMS 1034).

7.0 CONCLUSIONS

We performed an extensive literature review of rate constants used in the CB6r4 mechanism that considered 152 of the 233 reactions in CB6r4. We revised reaction rates for 47 reactions and added one new reaction to create CB6r5. CB6r5 tends to predict higher ozone concentrations than CB6r4 although CB6r5 has lower ozone over portions of the Gulf of Mexico. Chemically, the ozone changes due to CB6r5 updates are associated with small changes (increases) in NO_2 in regions where ozone production is NOx-limited. Accordingly, we conducted additional review of mechanism updates that influence NO_2 availability leading to a revised final mechanism (development version 3, CB6r5d3) with more moderate ozone increases than the initial version (CB6r5d1). Quantitative performance evaluation for 8-hour average ozone in June 2012 found that CB6r5 performs similarly to CB6r4 with statistical metrics (NMB, NME, and r) for both mechanisms meeting the criteria recommended by Emery et al. (2017). The tendency of CB6r5 to predict slightly higher ozone than CB6r4 produced slightly more positive bias and larger error with CB6r5 than CB6r4. However, the ozone changes associated with CB6r5 updates are too small for ozone model performance evaluation to assess their validity, when taking into consideration that models have uncertainties other than the chemistry (Dunker et al., 2020) including emissions, boundary concentrations, deposition and meteorology. We recommend additional testing and evaluation to understand how CB6r5 mechanism updates influence CAMx model performance for ozone.

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Supplemental Information

Table S - 1. CB6r4 Model performance statistics for 8-hour average O_3 from 11 AM to 7 PM at Continuous Ambient Monitoring Stations in Texas in June 2012.

Site (CAMS)	Number of Observations	Average Concentration - Observations (ppb)	Average Concentration - Model (ppb)	R^2	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias (%)	Normalized Mean Error (%)	Mean Fractional Bias (%)	Mean Fractional Error (%)
ANWC (C3)	27	48.3	52.6	0.902	4.31	7.1	8.93	14.7	11.7	16.2
ARLA (C61)	30	53.5	58.6	0.902	5.11	6.99	9.55	13.1	12.3	14.7
ARPS (C659)	30	37	39.3	0.774	2.33	7.39	6.31	20	11.5	21.3
ATAS (C560)	29	44.4	53.4	0.792	9.06	10.6	20.4	23.8	21.6	23.7
AUDU (C38)	30	49	54.1	0.902	5.11	6.17	10.4	12.6	12	13.9
BAYP (C53)	29	46.8	54.7	0.865	7.92	10.3	16.9	21.9	22.6	25.5
BMTC (C2)	30	46.2	51.5	0.792	5.21	7.55	11.3	16.3	14.2	18.7
BOER (C58)	29	54.1	54.6	0.846	0.485	5.37	0.897	9.92	2.33	10.3
BUHV (C562)	30	48	55.6	0.81	7.55	9.94	15.7	20.7	19.7	23.2
BVES (C503)	29	45.8	52.8	0.81	6.92	7.75	15.1	16.9	16.3	17.6
BYTE (C1017)	23	42.8	49.8	0.846	7	8.16	16.4	19.1	19.2	20.8
BYWC (C552)	29	43.2	49.7	0.792	6.52	8.69	15.1	20.1	18.9	22.4
CALA (C59)	26	40.8	48.2	0.884	7.34	7.68	18	18.8	18.6	19.4
CCHR (C660)	30	35.8	39.8	0.74	4.01	8.83	11.2	24.7	16.5	26.1
CCTO (C21)	8	29.4	36.9	0.672	7.5	8.12	25.5	27.6	24.4	25.6
CCWT (C4)	27	32.8	38.5	0.624	5.7	9.21	17.4	28.1	20.8	28.8
CLEB (C77)	21	56.9	59.5	0.865	2.62	5.96	4.61	10.5	6.43	11.3
CLHS (C572)	29	45.5	50.7	0.846	5.21	9.38	11.4	20.6	18.5	24.3
CLTN (C403)	28	43.2	52.3	0.846	9.05	11.7	20.9	27.2	26.5	29.7
CNR2 (C78)	30	47.6	54.3	0.672	6.75	8.54	14.2	18	15.3	18.5
COGR (C505)	29	39.5	48.9	0.865	9.41	9.61	23.8	24.3	25.9	26.1
COLE (C624)	29	38.9	44.8	0.74	5.91	7.29	15.2	18.8	15.6	19
CRBL (C553)	29	43.5	50.9	0.792	7.34	8.7	16.9	20	18.6	20.7
CRSA (C1051)	30	48.8	53	0.828	4.28	6.88	8.77	14.1	11	14.9
DALN (C63)	30	56.2	58.4	0.846	2.16	6.55	3.84	11.6	6.16	12.7

Site (CAMS)	Number of Observations	Average Concentration - Observations (ppb)	Average Concentration - Model (ppb)	R^2	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias (%)	Normalized Mean Error (%)	Mean Fractional Bias (%)	Mean Fractional Error (%)
DENN (C56)	28	57.8	60.6	0.922	2.76	5.23	4.77	9.04	6.48	9.96
DHIC (C401)	27	53.2	57.1	0.902	3.88	7.53	7.3	14.2	11	16.2
DNCG (C618)	28	40.6	45.4	0.902	4.84	7.02	11.9	17.3	17.4	20.8
DRIP (C614)	29	46.4	50.9	0.884	4.48	5.61	9.65	12.1	10.8	13
DRPK (C35)	30	45.6	52.2	0.81	6.6	9.53	14.5	20.9	19.5	23.3
ECES (C501)	29	44.6	48.9	0.846	4.3	5.92	9.64	13.3	11	13.8
EMTL (C75)	27	52.5	57.1	0.902	4.59	6.55	8.74	12.5	11.2	13.9
FAYT (C601)	30	42.3	47.5	0.902	5.26	6.35	12.4	15	14.5	16.4
FORH (C502)	29	48.9	54.7	0.846	5.76	6.46	11.8	13.2	12.4	13.9
FRIC (C31)	30	58.8	58.4	0.846	-0.367	5.32	-0.625	9.06	1.02	9.35
FWCB (C570)	30	46.2	49.6	0.865	3.4	8.66	7.37	18.8	14.3	21.9
FWMC (C13)	30	48.3	59	0.902	10.7	10.9	22.1	22.5	23.3	23.6
GALV (C1034)	30	38.3	52.4	0.846	14.1	14.1	36.8	36.8	36.1	36.2
GRAN (C73)	15	53.2	54.5	0.706	1.33	5.86	2.51	11	4.09	11.5
GRAP (C70)	29	58.7	60.1	0.884	1.42	6.08	2.41	10.4	4.87	11.2
GRVL (C1006)	30	49.5	51.7	0.865	2.2	5.27	4.44	10.6	6.54	11.8
H03H (C603)	29	46.8	52.2	0.828	5.46	9.09	11.7	19.4	17.2	22.3
HALC (C8)	29	45.5	53.9	0.81	8.46	10	18.6	22	20.1	22.3
HCHV (C15)	30	44.9	51.8	0.846	6.87	8.29	15.3	18.5	18.9	21
HCQA (C409)	26	50	54.9	0.902	4.87	8.31	9.74	16.6	15.7	19.6
HLAA (C408)	28	48.7	55.7	0.792	6.95	8.62	14.3	17.7	16.4	18.6
HNWA (C26)	27	48.5	55.8	0.828	7.3	8.97	15.1	18.5	17.9	20.2
HOEA (C1)	28	46.7	53	0.81	6.27	10.6	13.4	22.8	18.6	24.4
HROC (C81)	21	38.6	50.8	0.828	12.3	13.8	31.8	35.7	34.4	36.2
HSMA (C406)	29	46.4	51.2	0.846	4.8	8.77	10.3	18.9	15.8	20.7
HTCA (C411)	27	48.5	54.4	0.865	5.91	8.51	12.2	17.5	16	19.2

Site (CAMS)	Number of Observations	Average Concentration - Observations (ppb)	Average Concentration - Model (ppb)	R^2	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias (%)	Normalized Mean Error (%)	Mean Fractional Bias (%)	Mean Fractional Error (%)
HTMS (C622)	30	44.4	48.1	0.846	3.76	6.61	8.46	14.9	10.8	15.8
HUFM (C563)	30	47.1	50	0.757	2.86	5.35	6.07	11.4	7.55	11.9
HUTO (C6602)	29	43.5	49	0.902	5.5	6.09	12.7	14	14.4	15.4
HWAA (C405)	29	43.6	54.9	0.774	11.3	12.5	25.9	28.6	28.7	30.3
INEZ (C609)	8	37.1	42.1	0.689	5.01	7.62	13.5	20.6	14.9	21.1
ISID (C685)	30	33.3	39	0.774	5.62	8.06	16.9	24.2	20.8	26.2
ITLY (C1044)	30	45.6	52.2	0.922	6.6	7.24	14.5	15.9	16.6	17.7
JEFC (C64)	29	46.7	49.5	0.828	2.76	7.29	5.9	15.6	10.8	17.4
KARN (C85)	30	50.4	54	0.757	3.58	6.76	7.11	13.4	9.54	14.9
KATP (C559)	28	43.6	54.1	0.828	10.4	10.4	23.9	23.9	24.6	24.6
KAUF (C71)	30	50.3	51.2	0.902	0.848	4.53	1.68	9	3.57	9.53
KELC (C17)	30	55.5	60	0.884	4.48	6.62	8.07	11.9	10.2	13.2
LGTN (C690)	28	49.3	53.7	0.884	4.37	5.9	8.85	12	10.5	13
LGVW (C19)	28	49.3	53.8	0.81	4.41	6.73	8.94	13.6	11.5	15.7
LKJK (C1016)	30	40.1	45.6	0.865	5.54	8.53	13.8	21.3	20.3	25
LPSB (C556)	30	45.6	52.1	0.828	6.55	9.01	14.4	19.8	17.6	21.6
LYNF (C1015)	28	44.3	52.1	0.828	7.73	8.87	17.4	20	19.7	21.6
MACP (C84)	16	58.9	53.5	0.902	-5.41	10.6	-9.18	18	-2.58	17.9
MDLO (C52)	30	50.3	56.1	0.922	5.82	7.17	11.6	14.3	13.9	15.9
All Sites	**3012**	**46.1**	**51.5**	**0.828**	**5.43**	**7.98**	**11.8**	**17.3**	**15.2**	**19.3**

Table S - 2. CB6r5d3 Model performance statistics for 8-hour average O_3 from 11 AM to 7 PM at Continuous Ambient Monitoring Stations in Texas in June 2012.

Site (CAMS)	Number of Observations	Average Concentration - Observations (ppb)	Average Concentration - Model (ppb)	R^2	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias (%)	Normalized Mean Error (%)	Mean Fractional Bias (%)	Mean Fractional Error (%)
ANWC (C3)	27	48.3	53.3	0.902	5.08	7.23	10.5	15	13.1	16.7
ARLA (C61)	30	53.5	59	0.902	5.54	7.22	10.4	13.5	13.1	15.1
ARPS (C659)	30	37	38.7	0.792	1.73	7.14	4.68	19.3	9.96	20.6
ATAS (C560)	29	44.4	54	0.774	9.62	11	21.7	24.8	22.6	24.4
AUDU (C38)	30	49	55	0.902	5.95	6.6	12.1	13.5	13.5	14.7
BAYP (C53)	29	46.8	55.1	0.884	8.32	10.2	17.8	21.7	23.2	25.3
BMTC (C2)	30	46.2	51.8	0.792	5.54	7.75	12	16.8	14.5	18.9
BOER (C58)	29	54.1	55.1	0.865	1.03	5.25	1.9	9.71	3.28	10.2
BUHV (C562)	30	48	56.2	0.828	8.12	9.82	16.9	20.5	20.6	23.1
BVES (C503)	29	45.8	53.4	0.828	7.52	7.98	16.4	17.4	17.4	18.1
BYTE (C1017)	23	42.8	49.8	0.846	7.06	8.44	16.5	19.8	19.1	21.1
BYWC (C552)	29	43.2	49.7	0.81	6.52	8.72	15.1	20.2	18.7	22.2
CALA (C59)	26	40.8	48.6	0.902	7.79	7.93	19.1	19.4	19.4	19.8
CCHR (C660)	30	35.8	39.4	0.74	3.56	8.67	9.95	24.2	15.3	25.6
CCTO (C21)	8	29.4	36.5	0.624	7.05	8.09	24	27.5	23.2	25.4
CCWT (C4)	27	32.8	38	0.624	5.29	8.99	16.2	27.5	19.7	28.2
CLEB (C77)	21	56.9	60.2	0.865	3.26	6.23	5.73	10.9	7.54	11.8
CLHS (C572)	29	45.5	50.7	0.865	5.19	8.88	11.4	19.5	18.2	23.2
CLTN (C403)	28	43.2	52.5	0.846	9.34	11.7	21.6	27	26.8	29.6
CNR2 (C78)	30	47.6	55.1	0.672	7.53	9.12	15.8	19.2	16.8	19.6
COGR (C505)	29	39.5	49.4	0.865	9.92	9.99	25.1	25.3	26.8	26.9
COLE (C624)	29	38.9	44.8	0.74	5.92	7.34	15.2	18.9	15.4	18.9
CRBL (C553)	29	43.5	51.2	0.774	7.66	8.9	17.6	20.4	19	20.9
CRSA (C1051)	30	48.8	54.2	0.828	5.48	7.38	11.2	15.1	13.3	15.9
DALN (C63)	30	56.2	59	0.865	2.72	6.58	4.83	11.7	7.14	12.8

Site (CAMS)	Number of Observations	Average Concentration - Observations (ppb)	Average Concentration - Model (ppb)	R^2	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias (%)	Normalized Mean Error (%)	Mean Fractional Bias (%)	Mean Fractional Error (%)
DENN (C56)	28	57.8	61.1	0.922	3.26	5.34	5.64	9.23	7.3	10.2
DHIC (C401)	27	53.2	57.4	0.884	4.23	7.57	7.96	14.2	11.7	16.4
DNCG (C618)	28	40.6	45.3	0.902	4.72	6.66	11.6	16.4	16.8	20.1
DRIP (C614)	29	46.4	51.7	0.884	5.32	6.13	11.5	13.2	12.4	13.9
DRPK (C35)	30	45.6	52.3	0.828	6.73	9.39	14.8	20.6	19.5	22.9
ECES (C501)	29	44.6	49.2	0.846	4.63	5.87	10.4	13.2	11.6	13.8
EMTL (C75)	27	52.5	57.6	0.902	5.08	6.85	9.67	13	12.1	14.5
FAYT (C601)	30	42.3	48.2	0.902	5.94	6.54	14.1	15.5	15.9	16.9
FORH (C502)	29	48.9	55.3	0.865	6.4	6.79	13.1	13.9	13.5	14.4
FRIC (C31)	30	58.8	59	0.865	0.247	5.14	0.42	8.75	2.08	9.13
FWCB (C570)	30	46.2	49.7	0.884	3.45	8.09	7.46	17.5	14.1	20.8
FWMC (C13)	30	48.3	59.4	0.902	11.1	11.2	23.1	23.3	24.1	24.2
GALV (C1034)	30	38.3	51.8	0.846	13.5	13.5	35.2	35.2	34.7	34.7
GRAN (C73)	15	53.2	55.2	0.689	2.08	5.9	3.91	11.1	5.38	11.7
GRAP (C70)	29	58.7	60.6	0.884	1.88	6.16	3.2	10.5	5.63	11.4
GRVL (C1006)	30	49.5	52.8	0.865	3.3	5.46	6.66	11	8.64	12.3
H03H (C603)	29	46.8	52.6	0.846	5.78	9.02	12.4	19.3	17.6	22.1
HALC (C8)	29	45.5	54.4	0.81	8.97	10.4	19.7	22.8	21	22.9
HCHV (C15)	30	44.9	52.1	0.865	7.16	8.48	16	18.9	19.3	21.2
HCQA (C409)	26	50	55.3	0.922	5.26	8.09	10.5	16.2	16.1	19.2
HLAA (C408)	28	48.7	56.3	0.828	7.54	8.78	15.5	18	17.4	19
HNWA (C26)	27	48.5	56.6	0.846	8.11	9.44	16.7	19.5	19.3	21.2
HOEA (C1)	28	46.7	53.4	0.81	6.7	10.7	14.3	23	19.2	24.5
HROC (C81)	21	38.6	51.1	0.828	12.6	13.9	32.6	36	34.7	36.3
HSMA (C406)	29	46.4	51.3	0.846	4.96	8.53	10.7	18.4	15.8	20.1
HTCA (C411)	27	48.5	54.9	0.865	6.41	8.54	13.2	17.6	16.7	19.3

Site (CAMS)	Number of Observations	Average Concentration - Observations (ppb)	Average Concentration - Model (ppb)	R^2	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias (%)	Normalized Mean Error (%)	Mean Fractional Bias (%)	Mean Fractional Error (%)
HTMS (C622)	30	44.4	48.6	0.846	4.19	6.61	9.44	14.9	11.7	15.8
HUFM (C563)	30	47.1	50.4	0.757	3.26	5.49	6.93	11.7	8.25	12.1
HUTO (C6602)	29	43.5	49.8	0.902	6.31	6.59	14.5	15.2	16	16.5
HWAA (C405)	29	43.6	55.4	0.792	11.8	12.7	27	29.2	29.4	30.7
INEZ (C609)	8	37.1	42.3	0.722	5.28	7.39	14.3	19.9	15.4	20.6
ISID (C685)	30	33.3	38.5	0.792	5.14	7.74	15.4	23.2	19.6	25.3
ITLY (C1044)	30	45.6	52.9	0.922	7.38	7.8	16.2	17.1	18.1	18.7
JEFC (C64)	29	46.7	49.5	0.846	2.81	7.17	6.01	15.3	10.5	17
KARN (C85)	30	50.4	55.3	0.757	4.93	7.2	9.79	14.3	12	15.7
KATP (C559)	28	43.6	54.6	0.828	11	11	25.1	25.1	25.4	25.4
KAUF (C71)	30	50.3	52.3	0.902	1.93	4.76	3.84	9.45	5.67	10.1
KELC (C17)	30	55.5	60.5	0.884	4.97	6.81	8.95	12.3	11	13.6
LGTN (C690)	28	49.3	54.4	0.884	5.07	6.34	10.3	12.9	11.7	13.8
LGVW (C19)	28	49.3	55.1	0.81	5.74	7.43	11.6	15.1	13.9	16.9
LKJK (C1016)	30	40.1	45.4	0.884	5.37	7.94	13.4	19.8	19.6	23.6
LPSB (C556)	30	45.6	52.1	0.828	6.47	9	14.2	19.7	17.3	21.4
LYNF (C1015)	28	44.3	52.2	0.846	7.9	8.95	17.8	20.2	19.8	21.6
MACP (C84)	16	58.9	53.6	0.902	-5.32	10.1	-9.04	17.2	-2.83	17.2
MDLO (C52)	30	50.3	56.6	0.922	6.35	7.43	12.6	14.8	14.9	16.4
All Sites	3012	46.1	51.9	0.828	5.82	8.05	12.6	17.5	15.8	19.3